055.1.014

Volume VIII] JANUARY, 1931 [No. 1

Journal
of the
Indian Chemical Society

Contents

		Page
1.	Gasification of Water Hyacinth (*Eichornia Crassipes*).—By Hemendra Kumar Sen and Harendra Nath Chatterjee	1
2.	Studies in Quinoline Compounds. Part III.—By Upendra Nath Brahmachari and Tarapada Bhattacharjee ...	7
3.	Studies in the Coagulation of Colloids from the Standpoint of Smoluchowski's Theory. Part I. Coagulation of Antimony Sulphide Sol.—By Shridhar Sarvottam Joshi and S. Madhava Prabhu	11
4.	Use Phenolic Acids in the Detection, Separation and Estimation of Metals. Part V. Separation of Copper from Cadmium and their Subsequent Estimations.—By Pabitra Nath Das-Gupta and Haribola Saha ...	19
5.	Chemical Examination of the Roots of *Hygrophyla Spinosa*.—By Narendra Nath Ghatak and Sikhibhushan Dutt	23
6.	Mercury Acetamide as Mercurating Agent.—By K. G. Naik and L. D. Shah	29
7.	Reactivity of Conjugated Systems. Part III. Condensation of $\alpha:\beta$—Unsaturated Esters with Cyanoacetamide.—By Chittaranjan Barat	37
8.	Formation of the Sodium Derivatives of Compounds Containing Reactive Methylene Group.—By K. G. Naik and L. D. Shah	45

All communications to be addressed to the Secretary, Indian Chemical Society, 92, Upper Circular Road, Calcutta.

Cost of Single Issue, Rs. 2

Annual Subscription for { **Non-Fellows, Rs. 16** / **Fellows, Rs. 15**

Printed at the Calcutta University Press, Senate House, Calcutta, by Bhupendralal Banerjee and published by P. C. Mitter, Esq., M.A., Ph.D., Secretary, Indian Chemical Society.

18,645.

Council of the Indian Chemical Society

President:
B. K. Singh, Sc.D., F.I.C., I.E.S.

Vice-Presidents:
(Who have filled the Office of President)
Sir P. C. Ray, Kt., C.I.E., Ph.D., D.Sc.
Gilbert J. Fowler, D.Sc., F.I.C.

Vice-Presidents:
U. N. Brahmachari, M.A., M.D., Ph.D.
N. R. Dhar, D.Sc., F.I.C., Dr.ès. Sc.
S. S. Bhatnagar, D.Sc., F.Inst.P.

Secretary:
P. C. Mitter, M.A., Ph.D.

Treasurer:
R. N. Sen, M.A., M.Sc., I.E.S.

Editors:
J. N. Mukherjee, D.Sc.
K. G. Naik, D.Sc., F.I.C.

Members of the Council:
B. B. Dey, D.Sc., F.I.C.
H. B. Dunnicliff, Sc.D., F.I.C.
J. C. Ghosh, D.Sc.
K. H. Hassan, M.Sc., L.Ag.
D. D. Karve', M.Sc., Ph.D.
S. D. Muzaffer, M.A., Ph.D.
P. Neogy, M.A., Ph.D., I.E.S.
P. R. Ray, M.A.
Rev. Father J. Van Neste, S.J.
Rao Bahadur M. R. Ramaswami Sivan, B.A., Dip. Agrl.
Mata Prasad, D.Sc.
H. E. Watson, D.Sc., F.I.C.

Committee of Publication.
S. S. Bhatnagar, D.Sc., F.Inst.P.
N. R. Dhar, D.Sc., F.I.C., Dr.ès. Sc.
J. C. Ghosh, D.Sc.
P. R. Ray, M.A.
H. K. Sen, D.Sc., D.I.C.
P. C. Speers, M.A.
J. N. Mukherjee, D.Sc.
K. G. Naik, D.Sc., F.I.C.
P. C. Mitter, M.A., Ph.D.
R. N. Sen, M.A., M.Sc., I.E.S.
} *Ex-officio.*

Hony. Auditors:
T. K. Rai Chaudhury, B.Sc., L.L.B., A.C.A.
P. C. Nandi, M.A., B.Sc., A.C.A.
(Chartered Accountants)

Asstt. Editors:
P. K. Bose, D. Sc.
S. K. Majumdar, M.Sc.

Asstt. Secretary:
G. Banerjee, M.Sc.

CUL-H00468-1-18645
JCU898
18,645
309
1

Gasification of Water Hyacinth (*Eichornia Crassipes*).

By Hemendra Kumar Sen and Harendra Nath Chatterjee.

In continuation of our work already published (Sen, Pal, and Ghosh, *J. Indian Chem. Soc.*, 1929, **6**, 673), it was considered of interest to investigate the technical gasification of this plant in view of its abundant growth in certain tropical non-saline waters. According to a report of the Special Officer appointed by the Government of Bengal, the plant spreads over an area of 4269 sq. miles in Bengal alone, choking many important waterways, and causing great agricultural loss. Pending any effective method of eradicating the pest rapidly, the question of utilisation naturally deserves consideration. Three methods of utilisation of this weed have been investigated in this laboratory, an account of which is recorded below:

(1) *Saccharification* by acid digestion and subsequent *fermentation* has already been described (*loc. cit.*). This aspect of the problem assumes more than ordinary interest in view of the publication of the Scholler Patent in June, 1929 (B. P. 278,317), which claims a practically quantitative conversion of cellulose into fermentable sugar by means of pressure percolation with dilute sulphuric acid.

(2) *Gasification of Water Hyacinth by Air and Steam.*—This process is essentially similar to that attempted elsewhere for the utilisation of peat. Water hyacinth is an aquatic plant characterised by a very high percentage of water content like that of peat, as much as 95% when fresh. The nitrogen content is also

almost similar to that of peat, being mostly over 2%. The ash content is much higher, reaching up to 22% at times of which 55 to 60% is practically pure potassium chloride. This renders recovery-distillation more economical. A pound of steam-oven dried sample has a calorific value of 6530 B. T. U., whilst the ordinary sun-dried sample containing approximately 16% moisture has a calorific value of 5580 B. T. U. The plant will, therefore, bear no profitable gasification with more than 80% water content as the whole of the fuel value of the plant would then be used up in evaporating and super-heating the water contained therein. Mere sun-drying reduces the moisture content to 16°/₀. This is quite comparable to the working at Orentano in Italy where the peat is reported to have been brought to the producers with 30—35°/₀ water. With this water content there appears to be efficient working. Frank claims that peat containing up to 50°/₀ water can be treated in Mond producers to yield 70—80°/₀ of its nitrogen as ammonium sulphate (*Chem. Ztg.*, 1908, **32**, 580). Caro and Frank (*Z. angew. Chem.*, 1910, **23**, 1844) go still further and consider even 60°/₀ water content as being workable. Haanel (*Canada Dept. of Mines, Mines Branch, Ottawa, Bulletin No.* 154) whose critical review in this direction is very important, opposes this figure, and maintains that "under the most ideal conditions—which do not and cannot obtain in actual practice—the quantity of heat generated by the burning of such peat is not sufficient to effect the various reactions and provide for losses and simultaneously give a power gas of the heating value claimed."

Our laboratory experiments were performed with sun-dried water hyacinth containing approximately 16°/₀ moisture, which is about the condition in which it is available after a fortnight's stacking in the sun. A silica tube was at first wrapped up with a few layers of asbestos paper, and then wound round with nichrome wire. The tube was enclosed in a wider sheet-iron casing, the annular space being packed with well-ignited magnesia. The outer casing was finally covered with a thick sheet of asbestos board in order to prevent quick radiation. Such a furnace lasted on an average 20 to 30 heatings up to 980°. The silica tube carried a thermocouple at one end reaching almost to the middle in order to ensure a fairly accurate average temperature prevailing at the time of the experiment. The introduction of air and steam was effected from the other end of the silica tube by means of an aspirator working on the

distillate end as shown in Fig. 1. The volume of water delivered by

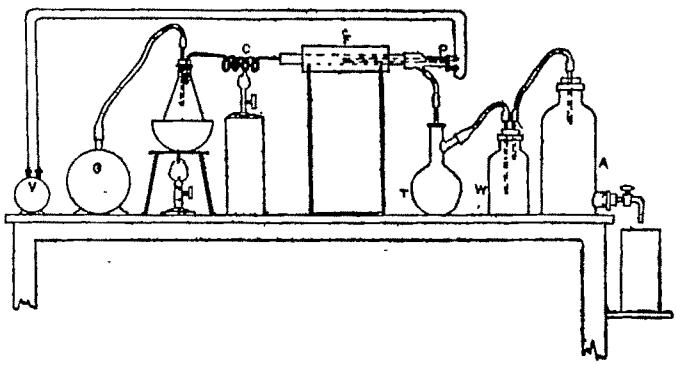


FIG. 1.

G, gasometer; C, superheating coil; F, electric furnace;
W, sulphuric acid wash-bottle; A, aspirator bottle; P, pyrometer; T, tar-catcher.

the aspirator during the experiment was necessarily equivalent to the volume of gas collected whilst the gasometer, *G*, indicated the volume of air introduced in the particular experiment. The receiver, *T*, and the sulphuric acid washer, *W*, retained any ammoniacal vapours generated in course of the gasification. Their contents were afterwards distilled with alkali, the volatile base absorbed in standard acid and expressed as ammonia. The volume of gas obtained per ton of sun-dried water hyacinth works out at approximately 40,000 cft., having under working conditions a calorific value of 142 B.T.U. The ammonium sulphate was on an average 100 pounds to the ton of water hyacinth. The residue after gasification is a dull grey ash, quite loose if the temperature is not allowed to exceed 1000°. This mass on extraction with water and evaporation of the solution, yields 2 cwts of potassium chloride of 95°/₀ purity.

Below are given the results of a few of the numerous experiments on gasification:

Water hyacinth used (in grams)	100	100	100	100
Furnace temperature	720—730°	720—730°	800—810°	960—980°
Air saturation temperature	75°	80°	70°	75°
Air volume	3·9 cft.	3·75 cft.	3·25 cft.	3·3 cft.
Time of gasification	3 hrs. 13 mins.	1½ hrs.	3 hrs.	1½ hrs.
Ammonia	1·17	0·94	0·82	

Water hyacinth used (in grams)	100	100	100	100
Volume of gas collected (in litres)	130	134	138	135
Hydrogen (per cent.)	12	16·14	16·6	19·7
Methane (per cent.)	1·2	1·5	4·8	nil
Carbon monoxide (per cent.)	14·03	12·8	21·7	22·1
Carbon dioxide (per cent.)	5·0	6·5	4·1	3·4
Nitrogen (per cent.)	67·0	—	52·8	—

Calculating from the blast saturation temperature of 75—80° we find that 39g. of moisture are carried over for every 100 g. of water hyacinth, or 0·39 ton of steam per ton of air-dried water hyacinth. Carbon dioxide is evidently less, as some of it must have dissolved in the aspirator water at 31°.

(3) *Bacterial Decomposition of Water-Hyacinth.*—The fairly large quantity of hemi-cellulose in the weed naturally suggested the possibility of utilising the weed by bacterial fermentation. Some preliminary experiments were already published (Sen, Pal, and Ghosh, *loc. cit.*), and since the appearance of a controversy between Fowler and Weston in a local trade journal (*Minutes of the Proceedings of the Institute of Civil Engineers*, Vol. 226, p. 32. *The Capital*, 1929, Vol. 83, pp. 482, 602) the question has been subjected to a more critical investigation. These results are given below:

The green water hyacinth as it is collected from canals or large tanks, contains 95°/₀ water, about 4°/₀ organic matter, and 1°/₀ mineral matter. This is first of all macerated by pounding in an iron vessel by a pestle to small shreds, and the whole carefully transferred to a large and tall winchester bottle (3 litres capacity usually) containing sewage of a definite volume. The water content of the plant taken was separately determined in an equivalent sample in order to allow for it in subsequent calculations. No special precaution for maintaining constant temperature was taken. The temperature between March and April was usually 32° in the laboratory. All experiments were checked against controls, and gas volumes were corrected accordingly. A typical result is given below:—

196 Grams of green water hyacinth containing 80 per cent. moisture gave with $\frac{3}{4}$ litre sewage the following volumes of gas.

	Gas collected.	Control.
First day (24 hrs.)	1875 c.c.	500 c.c.
Second day	3750	500
Third day	4320	500
Fourth day	3100	350
Fifth day	3100	300
Sixth day	2600	200
Seventh day	2100	150
Eighth day	1560	100
Ninth to twelfth day	3650	200
Thirteenth to fifteenth day	1100	120
Total gas collected	27,155 c.c.	2,920 c.c.

Surplus gas due to the fermentation of water hyacinth (196 g.)=24,235 c.c. collected over water at 31°. 196 G. of 80% moist water hyacinth correspond to 39·2 g. of dry matter of which 16·4 g. correspond to α-, β-, and γ- celluloses. Roughly speaking, therefore, for every gram of total cellulose together with its attendant lignin and other organic matters, 1475 c.c. of gas of the average composition, CO_2=22·1%, O=1·2%, CH_4=51·6%, H=25·4% were collected. Towards the end on the tenth day the composition of the gas varied considerably, giving decidedly larger volumes of methane and little of hydrogen:

Methane	70%
Hydrogen	3·8
Carbon dioxide	25·2
Nitrogen and oxygen, by diff.	1·0

This would point to an independent methane—carbon dioxide fermentation as has been observed by some workers before.

Whilst the fermentability of smashed green hyacinth is great, that of the dry plant is distinctly sluggish. This, improves, however, on the dry plant being digested under heat and pressure with slightly acidulated water. The yield of gas is still far less, being about half of that obtained from the green material. So far, under best possible conditions of working, 26,500 cft. of gas per 20 tons of green water hyacinth (1 ton of dry material), having a calorific value of 602 B. T. U. have been obtained. On several occasions much smaller values, as low as half of this has been

recorded. In no case, however, the fermentation entirely stopped until after 8 weeks.

In order to ascertain whether the gas produced from lignocellulose fermentation is fundamentally different from that evolved in the bacterial decomposition of pure cellulose, 5 g. of the best Swedish filter paper were treated with $\frac{2}{3}$ litre of the same sewage with the following results:—

	Gas collected.	Control.		Gas collected.	Control.
First day (24 hours)	500 c.c.	250 c.c.	Seventh day	500 c.c.	75 c.c.
Second day	1000	250	Eighth to tenth day	650	50
Third day	1000	250	Eleventh to fifteenth day	600	75
Fourth day	850	150			
Fifth day	750	100			
Sixth day	500	75	Total	6350 c.c.	1275 c.c.

The total gas from 5 g. of filter paper, therefore, is 5075 c.c. or approximately 1000 c.c. per g. of cellulose, The average composition of this gas mixture is somewhat different, being poorer in hydrogen.

Methane	79·2 per cent.
Carbon dioxide	15·0
Hydrogen	2·7
Nitrogen	3·1

Whether this decided poverty of hydrogen in pure celluose fermentation is due to the absence of other secondary groups which are so largly present in lignocelluloses need not be entered upon here.

Further work in this direction is already in progress.

Received December 23, 1929.

DEPARTMENT OF APPLIED CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

Studies in Quinoline Compounds. Part III.

By Upendra Nath Brahmachari and Tarapada Bhattacharjee.

The fact that certain derivatives of quinoline ("plasmochin") and certain arsenicals possess antimalarial properties, led us to synthesise some arsenic derivatives of quinoline. The first idea that would strike a worker in this direction is to attempt to introduce arsenic directly into the quinoline nucleus. Up till now, such a method has not been found feasible except in the case of quinaldine (Frankel and Lowy, *Ber.*, 1913, **46**, 2549). The compound has been obtained indirectly by the application of Döbner —Miller's reaction to *p*-aminophenylarsonic acid.

With the view of introducing arsenic directly into derivatives of quinoline we first tried the method of Bart (German Patent, 250264) as well as Mouneyrat's modification of it (British Patent, 142947). In all our attempts we obtained dyes and reduction products only. No compound containing arsenic was isolated during a prolonged investigation in this direction.

We next tried the mercuric acetate method, but here we found that during the course of the reaction the mercury was almost quantitatively reduced to the metallic state.

Subsequently we tried to condense aminoquinolines with aromatic arsenicals. With this object, chloroacetyl-*p*-arsanilic acid was condensed with various aminoquinolines, following the method of Jacobs and Heidelberger (*J. Amer. Chem. Soc.*, 1919, **41**, 1810). The compounds enumerated below were thereby obtained:—

(1) Quinoline-8-aminoacetyl-*p*-arsanilic acid.
(2) 6-Methoxyquinoline-5-aminoacetyl-*p*-arsanilic acid.
(3) Quinoline-6-aminoacetyl-*p*-arsanilic acid.
(4) 2-Methylquinoline-6-aminoacetyl-*p*-arsanilic acid.

These compounds are generally yellow in colour. They are insoluble in water, very sparingly soluble in common organic

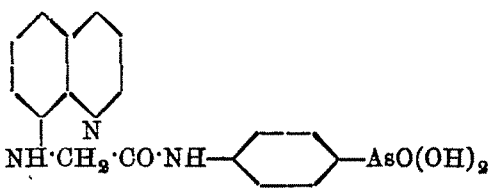
solvents such as alcohol, ether, acetone, etc. They however dissolve very easily in aqueous caustic alkalis. From the alkaline solutions, acids precipitate the original compound. Continued boiling with dilute alkali causes hydrolysis. They are sparingly soluble in dilute mineral acids.

On treating with an excess of sodium nitrite solution in 50% acetic acid suspension beautiful crystalline nitroso-derivatives are obtained.

For the sake of examining the therapeutic properties we also prepared arsanilic acid salts of 8- and 6-aminoquinolines.

Experimental.

Quinoline-8-aminoacetyl-p-arsanilic Acid.



Chloroacetylarsanilic acid (2·26 g.), prepared according to Jacob and Heidelberger's method (*loc. cit.*), is dissolved in *N*-sodium hydroxide solution (7·5 c.c.) and to it is added 8-aminoquinoline (1·6 g. in 7·5 c.c. alcohol). This mixture is then boiled on a water-bath for ½ hour. The solid which separates out is collected, washed with very dilute hydrochloric acid and then with water. It is then dried in vacuum. The compound has a deep yellow colour. It dissolves very easily in aqueous alkalis, diethylamine and also in concentrated hydrochloric acid. It is very difficultly soluble in all other solvents; m. p. 171° (decomp.). (Found: N, 10·2; As, 18·2. $C_{17}H_{16}O_4N_3As$ requires N, 10·5; As, 18·7 per cent.).

The *sodium salt* of the above compound is prepared by dissolving the moist acid in the smallest quantity of *N*-sodium hydroxide and then precipitating with an excess of alcohol. It is very easily soluble in water.

The *nitroso-derivative* is prepared by suspending 1 g. of the acid in 10 c.c. of 50% acetic acid and then treating with a solution of 1 g of sodium nitrite. On scratching the solution, the nitroso-compound separates. It has got a greenish-yellow colour. It

decomposes with effervescence at about 182°. (Found: N, 12·8. $C_{17}H_{15}O_5N_4As$ requires N, 13·00 per cent.).

6-Methoxyquinoline-5-aminoacetyl-p-arsanilic Acid.

The compound is prepared from 6-methoxy-5-aminoquinoline and chloroacetyl-*p*-arsanilic acid, the procedure being the same as in the case of the above compound. It has a dirty grey colour. It is easily soluble in alkalis but sparingly in all other solvents. It does not melt even at 240°. (Found: N, 9·5. $C_{18}H_{18}O_5N_3As$ requires N, 9·7 per cent.).

The *sodium salt*, prepared as indicated above, is very easily soluble in water.

The *nitroso-derivative* is an almost white substance and does not melt at 240°. (Found: N, 12·1. $C_{18}H_{17}O_6N_4As$ requires N, 12·2 per cent.).

Quinoline-6-aminoacetyl-p-arsanilic Acid.

This compound is prepared from 6-aminoquinoline and chloroacetylarsanilic acid in the usual manner.

It is a greenish-yellow powder, easily soluble in caustic alkalis, but practically insoluble in all organic solvents. It does not melt at 240°. (Found: N, 10·3. $C_{17}H_{16}O_4N_3As$ requires N, 10·5 per cent.). The *sodium salt* is prepared by dissolving the free acid in the smallest amount of dilute sodium hydroxide and then precipitating with alcohol. It is very easily soluble in water.

The *nitroso-derivative* melts above 240°. (Found: N, 12·7. $C_{17}H_{15}O_5N_4As$ requires N, 13·0 per cent.).

2-Methylquinoline-6-aminoacetyl-p-arsanilic Acid.

It is obtained from 2-methyl-6-aminoquinoline and chloroacetyl-*p*-arsanilic acid. In its properties it resembles the other compounds of the series. It does not soften below 240°. (Found: N, 9·7. $C_{18}H_{18}O_4N_3As$ requires N, 10·1 per cent.). The *sodium salt* prepared as usual is very easily soluble in water.

8-Aminoquinoline p-arsanilate.—This salt is prepared by mixing aqueous solutions of equimolecular quantities of 8-aminoquinoline hydrochloride and atoxyl. It separates out on scratching for some time. It is somewhat soluble in water. The compound decomposes

after a few days. It begins to soften from 210° but does not melt clearly at 240°.

6-*Aminoquinoline*-p-*arsanilate*.—This compound is similarly prepared from 6-aminoquinoline hydrochloride and atoxyl. It does not melt at 240°.

THE BRAHMACHARI RESEARCH INSTITUTE,
82/3, CORNWALLIS STREET, CALCUTTA.

Received December 9, 1930.

Studies in the Coagulation of Colloids from the Standpoint of Smoluchowski's Theory. Part I. Coagulation of Antimony Sulphide Sol.

By Shridhar Sarvottam Joshi and S. Madhava Prabhu.

The applicability of Smoluchowski's theory (*Z. Phys. Chem.*, 1917, **92**, 129) has been considered by most of the earlier workers with respect to the equation,

$$\Sigma n = n_0/1+\beta t, \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where n_0 denotes the original number of primaries and β the velocity constant. Σn gives the total number of particles in all stages of coalescence at the time t. The object of the present work was to examine another general result (*cf.* Anderson, *Trans. Faraday Soc.*, 1924, **19**, 628; also Freundlich and Basu, *Z. Phys. Chem.*, 1925, **115**, 203) of the above theory,

viz., $$\beta = \frac{1}{t}\left[\sqrt{n_0/n_t} - 1\right] \quad \ldots \quad \ldots \quad (2)$$

where n_t is the number of primaries in the coagulating sol at the time t.

Experimental.

The colloid was prepared by adding intermittently and with constant shaking a solution of tartar emetic to a large volume of twice-distilled water, saturated with hydrogen sulphide. The sol was much more stable than that obtained by leading H_2S in tartar emetic solution. This was found to be due to the precipitating action of small quantities of free antimonious acid produced in the latter case. After dialysing till free from acid, the sol was filtered and stocked in carefully cleaned and well stoppered hard-glass bottles. The colloid-content of the sol was determined by Kessler's method (*Pogg. Ann.*, 1868, **118**, 17). After the sol, the coagulator solution ($N/10$-H_2SO_4) and the reaction vessel had attained the thermostat

temperature, 25 c.c. of the coagulator solution were introduced simultaneously from two similar pipettes into the reaction vessel. After a definite time, the mixture was filtered, using a high grade analytical filter paper and the precipitate was washed with 20 c.c. of water. The time required for pipetting the solution in (7 sec.) and that for washing the precipitate (30 sec.) could be made practically constant. In these results a, $a-x$ denote respectively the colloid-content of the original sol and that of the coagulating sol at any time t, during coagulation. t, is exclusive of the time required for pipetting in and for washing the precipitate.

k, the bi-molecular constant and β, the Smoluchowski's constant were calculated from the values of $a-x$ read off from the curve A in fig. 1.

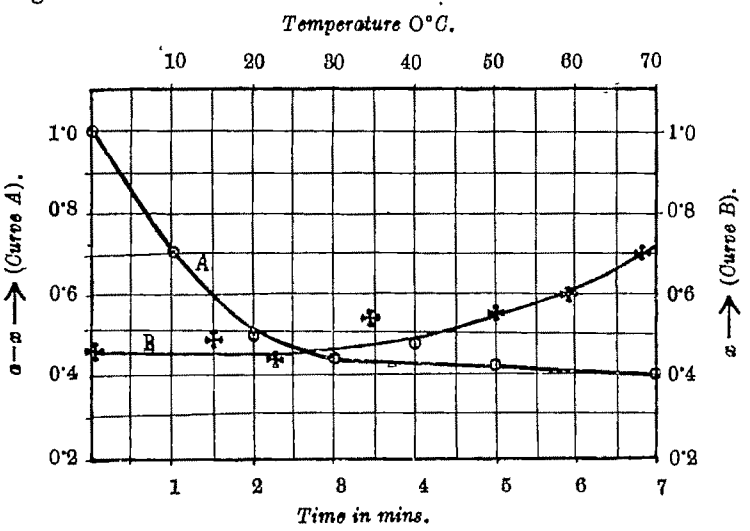


FIG. 1.

Same axes { Curve A, variation of $(a-x)$ with time.
Curve B, ,, ,, x wth temperature.

Influence of temperature on percentage of coagulation was studied in three series of experiments, the time (5 and 1·5 min.) being kept constant in each series (Table II and curve B in fig. 1). Viscosity of the coagulating sol was determined at different temperatures using an Ostwald's viscometer, 3, 5 and 7 min. after the start of coagulation. The corresponding densities were measured by means of a standard specific gravity bottle. The viscosity recorded in Table III represents mean of three independent readings.

TABLE I.

Temp. = 33°.

Initial colloid concentration = 0·124 g. Sb_2S_3 per litre.

10 c.c. $FeSO_4$ soln. = 0·01411 g. Sb_2S_3.

Time (min.).	Titre value for filtrate (c.c.).	$(a-x)$ in 50 c.c. of the mixture.	$a-x/a$	k	B
0	4·4	0·00621 (a)*			
1	3·1	0·00438	0·705	0·52	0·126
2	2·25	0·00318	0·512	0·45	0·18
3	2·0	0·00282	0·454	0·39	0·113
4	2·1	0·00296	0·477	0·32	0·124
5	1·9	0·00268	0·432	0·26	0·103
7	1·75	0·00247	0·398	0·22	0·09

TABLE II.

A.

Time of coagulation = 5 min.

0·27g. of Sb_2S_3 per litre. 10 c.c. of $FeSO_4$ soln. = 0·01547 g. Sb_2S_3.

Temp.	Titre (c.c.)	$(a-x)$ in 50 c.c. of mixture.	Percentage coagulation.
	4·1	0·00634 (a)*	—
34°	1·95	0·00302	52·4
,,	1·95	0·00302	52·4
50°	1·55	0·00239	62·3
,,	1·55	0·00239	62·3
70°	1·05	0·00162	74·4
,,	1·2	0·00185	70·7

B.

Time of coagulation = 1·5 min.

0·135g. of Sb_2S_3 per litre. 10 c.c. of $FeSO_4$ soln. = 0·0547g. Sb_2S_3.

Temp.	Titre (c.c.)	$(a-x)$ in 50 c.c. of mixture.	Percentage coagulation.
	4·4	0·00680(a)*	—
	4·35	0·00673(a)*	—
34°	2·3	0·00354	47·8
,,	2·25	0·00348	48·6
54°	2·15	0·00329	53·1
,,	2·05	0·00317	51·3

C. (*cf.* curve B, Fig. 1.)

Time of coagulation = 5·0 min. 0·2436 g. of Sb_2S_3 per litre.

0°	0·00328	46·2
14°·5	0·00312	48·9
23°·5	·00339	44·4
34°	0·00273	55·1
50°	0·00266	55·4
59°	0·00242	60·3
68°	0·00180	70·5

*a = Initial colloid-content.

TABLE III.

Temp.	x/a from fig. 1, curve B.	β	Viscosity of water. η_∞	Viscosity of colloid. η	Ratio, $\beta_T/\beta_{33°·5}$ with η_∞	with η	observed,
33°·5	0·52	0·0886	0·0072	0·00748	1·0	1·0	1·0
43°·5	0·54	0·0946	0·0062	0·00638	1·25	1·20	1·07
53°·5	0·57	0·105	0·00515	0·00574	1·55	1·39	1·18
62°	0·64	0·133	0·00458	0·00538	1·79	1·51	1·50
73°	0·75	0·2	0·0039	0·00484	2·17	1·73	2·26

Discussion of Results.

In applying equation (1) in general, the assumption is necessarily implied that a property like viscosity (Miyazawa, *J. Chem., Soc.*, Japan, 1912, **33**, 1179 ; Freundiich and Ishizaka, *Trans. Faraday Soc.*, 1918, **9**, 66 ; Gann, *Koll.-Chem. Beih.*, 1916, **8**, 65), or, relative transparency (Mukherjee and Majumdar, *J. Chem. Soc.*, 1924, **125**, 794 ; Desai, *Trans. Faraday Soc.*, 1928, **19**, 181), is a single-valued function of Σn. Since coalescence of particles is the chief effect in coagulation, its progress is best followed by employing a property depending upon the particle size. Thus Paine (*Koll. -Chem. Beih.*, 1912, **4**, 24) determined $a-x$, the uncoagulated part of a copper sol by separating the coagulum by stirring. In later work (Paine and Evans, *Trans. Faraday Soc.*, 1924, **24**, 649) a sample of the coagulating sol was heated quickly (which precipitated the coagulum), and a portion drawn off to measure $a-x$. Each of these methods is subject to an indeterminate correction, on account of the assumption regarding Σn metioned above. Whilst this would appear to be inevitable, especially in the case of polydisperse colloids, it is advantageous to examine the theory, using different methods of determining coagulation. This has been in progress for some time in these laboratories. The chief condition to be satisfied in employing any given property for measuring coagulation is that it shall vary continuously during coagulation without turning points. This is seen to be the case from curve A in Fig. 1. The amount of the coagulum determined at a given time during coagulation is therefore characteristic of the corresponding state of coagulation. Data given in Table II show that the degree of reproducibility of results for $a-x$ at different temperatures and for short intervals of time is good. Denoting by n_t, r, and ρ the number, the mean radius, and the density of the primaries at a time t, we get, $a-x=4/3\pi\rho(r_1^3 n_t + r'^3 n')$, where r' and n' refer to particles in a higher state of coalescence- $r'^3 n'$ is determined chiefly by the texture of the filter paper used. It is a measure of the average volume of particles at higher stages of coalescence. The number of particles at higher stages of coagulation has been assumed to be negligible as a first approximation. $a/a-x$ therefore, equals n_0/n_t involved in equation (2). More detailed results indicating the applicability of this method of measuring coagulation to other coagulating systems will be published shortly.

In Smoluchowski's theory, it is shown that the coagulation rate

exceeds that corresponding to a bimolecular reaction. It follows therefore, that in general, k, the bimolecular constant should increase with time in both rapid and slow coagulation. The results in Table I show just the opposite. Similar results were obtained by Anderson (*loc. cit.*) in the slow coagulation of gold sol. It is also seen from results in Table I that the constant β diminishes during coagulation. It is known in general, that the diminution of β with time is greater, slower the coagulation. In typical slow coagulation, β falls to a small fraction of the intial value soon after the start of coagulation. The observed decrease in β (about 20%) while 30% of the colloid has coagulated, shows that the rate is intermediate between the rapid and slow coagulations (*cf.* also Anderson, *loc. cit.*).

Results in Tables II, III (*cf.* also curve B, Fig. 1) show that the influence of temperature is more marked in the coagulation of the antimony sulphide than in that of the arsenious sulphide sol (Mukherjee, *J. Chem. Soc.*, 1920, **117**, 350). As regards the general influence of temperature on β, deducible from Smoluchowski's theory, Westgren and Reitstötter (*Z. Phys. Chem.*, 1918, **92**, 750) have shown that $\beta=\frac{RT}{N}\cdot\frac{n_0}{n_t}$ (3), where the different symbols have their usual significance. It follows therefore that $\beta_{T_1}/\beta_T = T/T_1 \cdot \eta_1/\eta$ (4) The results for this ratio given in Table III show that the agreement between theory and observation is but limited. The discrepancy between the two sets of values tends to diminish, when the viscosity of the colloid instead of that of water, is employed in calculating the ratio. In these results β contains implicitly the factor ϵ, which Smoluchowski employed to differentiate slow from rapid coagulation. ϵ denotes the probability of coalescence in a collision between two particles in the coagulating sol. It depends upon the surface density of the electrical charge on the particle and would diminish due to coalescence (Anderson. *loc. cit.*)producing a like variation in β (*cf.* Table I). The derivation of (4) from (3) necessitates that ϵ is independent of temperature. This is seen from the results of Freundlich and Basu (*loc. cit.*) and of Garner and Lewis (*J. Phys. Chem.*, 1926, **30**, 1401), who observed that equation (4) was applicable. It is however doubtful, if this can be in general true. It is more probable that the temperature variation of ϵ depends upon the chemical nature of the sol. Mukherjee and Papaconstantinou (*J. Chem. Soc.*, 1920, **117**, 1563) observed that ϵ might vary with

temperature due to its influence on the ionic adsorption, which determines the charge on the colloid particle. The difference between the observed and calculated values of the ratio β_T / β_{T_1} might be ascribed therefore in part to the above possibility.

CHEMICAL LABORATORIES,
BENARES HINDU UNIVERSITY,
BENARES.

Received, December 12, 1930.

Use of Phenolic Acids in the Detection, Separation and Estimation of Metals. Part V. Separation of Copper from Cadmium and their subsequent Estimations.

By Pabitra Nath Das-Gupta and Haribola Saha

When gallic acid and sodium or ammonium acetate are added to neutral or faintly acidic solutions of copper or cadmium salts, a voluminous chocolate brown precipitate is obtained in the case of copper, which is quantitative and in the case of cadmium no precipitate is formed (Das-Gupta, *J. Indian Chem. Soc.*, 1929, **6**, 631). These reactions have been studied further.

The precipitate with copper appears to be a definite compound, as on gently heating it gives a constant percentage of pure cupric oxide. The precipitate is soluble in mineral acids and in large excess of acetic acid. On heating it with sodium hydroxide, cuprous oxide is formed.

The precipitate is not of much use in estimating copper, as it is difficult to filter it through a Gooch crucible. The estimation is however much quicker, if the precipitate is dried, incinerated and weighed as CuO. This method is quite satisfactory in determining copper in presence of cadmium.

Experimental.

Faintly acidic solutions of copper and cadmium nitrates are separately made and copper and cadmium estimated by standard methods. Each c. c. of the copper and cadmium solutions contained 0·09883 and 0·09936 g. of Cu and Cd respectively.

A measured volume of the copper nitrate solution is taken in a beaker, diluted with water to a considerable volume, and excess of a 10% solution of ammonium acetate is added. The solution is

heated nearly to boiling and a freshly prepared saturated solution of gallic acid (1 %) is added drop by drop until the precipitation is complete. The voluminous precipitate is allowed to settle and filtered. The precipitate adhering to the side of the beaker is washed out into the filter with warm 2 % NH_4NO_3 solution. The precipitate is dried in the steam-oven (at higher temperature the substance attacks the filter) and ignited cautiously. The crucible is heated first gently over a low flame and then strongly for a few minutes when the precipitate is transformed to cupric oxide.

TABLE I.

Vol. of Cu soln. after dilution (c.c.).	Vol. of 10 % ammonium acetate soln. (c.c.).	Vol. of 1 % gallic acid soln. (c.c.).	CuO found (g.).	CuO present (g.).
25	15	25	0·1231	0·1237
35	,,	20	0·1236	
25	20	25	0·1234	
60	25	30	0·2468	0·2474
20	2	5	0·0244	0·02474
40	8	,,	0·0246	
15	* 3+5 c.c. 8 % NH_4NO_3 soln.	3	0·0122	0·01237
25	* 3+5 c.c. 8 % NH_4NO_3 soln.	,,	0·0121	

* Addition of ammonium nitrate helps coagulation of the precipitate.

Separation and Estimation of Copper and Cadmium when present together.

Measured volumes of copper and cadmium solutions are taken and as before, copper is precipitated by ammonium acetate and gallic acid. The copper precipitate is then washed by decantation with hot 2 % ammonium nitrate solution to free it from cadmium, which is tested in the filtrate by sulphuretted hydrogen. The copper precipitate is then dried and as before estimated as cupric oxide. In the filtrate, cadmium is first precipitated as cadmium sulphide, filtered, washed well with sulphuretted hydrogen water and estimated as cadmium sulphate. In this way with

JCU 898

different proportions of copper and cadmium solutions several estimations are made, which are given below.

TABLE II

Vol. of soln. containing Cu & Cd after dilution. (c.c.).	Vol. of ammonium acetate soln. (c.c.).	Vol. of 1% gallic acid (c.c.).	CuO found (g.).	CuO present (g.).	$CdSO_4$ found (g.).	$CdSO_4$ present (g.).
45	15	25	·1239	·1237	·1840	·1843
35	20	35	·1241	·1237	·1845	·1843
40	25	40	·2488	·2474	·1835	·1843
30	25	30	·1235	·1237	·3684	·3686
40	10	5	·0248	·0247	·3681	·3686
50	15	10	·0249	·0247	·3684	·3686
40'	25	40	·2477	·2474	·0368	·0368
45	30	35	·2482	·2474	·0369	·0368

In all the cases the cupric oxide and the cadmium sulphate are tested for possible contaminations of cadmium and copper respectively. In every case negative results are obtained.

Conclusion.

This method of separation and estimation of copper and cadmium can be claimed to be rapid and accurate. In the case of copper, this is also a more rapid and accurate gravimetric method; small amounts of copper can also be estimated gravimetrically by this method, as the precipitate obtained is very voluminous.

Our best thanks are due to the Indian Chemical Society for a Research grant to one of us (P.N.D.G.).

INORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
CALCUTTA.

Received December 8, 1930.

18,645.

Chemical Examination of the Roots of Hygrophyla Spinosa.

By Narendra Nath Ghatak and Sikhibhushan Dutt.

Hygrophyla Spinosa (Sanskrit—Kokilâksha, Bengali—Kuliámárá. Hindi—Tálmákhánâ) of the natural order of *Acanthaceæ*, is an annual marshy herb with an ascending rhizome and numerous stout, erect and unbranched stem, two to five feet long. The stems are somewhat compressed and thickened at the nodes with numerous long hairs below each node. The leaves are sessile and six at each node—the two outer ones 4—5 inches long and the four inner ones 1½ inches in length—each having a sharp yellow spine, one inch long. The flowers are bright blue in colour with an occasional white specimen, and generally eight at each node. The roots are creamy yellow in colour, thin, tapering and tubular, with numerous rootlets, possessing a peculiar marshy odour and a slimy cooling taste.

Hygrophyla spinosa has always occupied a prominent place in Hindu Materia Medica. The roots are considered to be cooling, diuretic, strengthening and stimulating and specially efficacious in dropsical cases and 'gravelish affections.' Mohammedan writers also mention the use of the plant for the same purpose and also for its external application in the form of a poultice or embrocation in rheumatism. In the Pharmacopoeia of India, several European writers also bear testimony to the excellent diuretic properties of the roots of the plant.

The roots were first examined by Warden (*Pharmacographica Indica*, Vol. III, p. 38), who by extraction with 80% alcohol, isolated a crystalline substance apparently in an impure form, which has been described as a mass of cauliflower-like nodules, nearly white in colour and contaminated with a trace of oil. It dissolved in concentrated sulphuric acid with a yellow colour.

The present investigation was undertake with a view to submit it to a thorough and systematic examination. The roots of the plant on extraction with rectified spirit and

subsequent distillation of the solvent yielded a crystalline substance contaminated with a sticky, green wax and a pale yellow oil. The waxy and oily impurities were eliminated by boiling the mass with saturated alcoholic potash and precipitation by water. The substance thus recovered on repeated crystallisations from dilute alcohol was obtained in the form of fine snow-white needles with silky lustre, melting at 194°. This substance was found to have the molecular formula $C_{28}H_{46}O$, and gave all the reactions of phytosterols. Thus it must be a member of the phytosterol family having the general formula $C_nH_{2n-10}O$, of which only one isolated example appears to exist in literature containing twentyeight carbon atoms, *viz.*, that furnished by Henry (*J. Chem. Soc.*, 1920, 117, 1624), who claims to have isolated a phytosterol $C_{28}H_{46}O$, from *Hyenanche globosa*.

The properties of the phytosterol isolated by the present authors in course of this investigation are quite in line with the general properties of the phytosterols of the above family and so evidently it is quite different from the phytosterol isolated by Henry which had a negative rotation $[\alpha]_D^{15} = -22{\cdot}4°$. Thus it gave an acetyl derivative melting at 208° and having a rotation of $[\alpha]_D^{28} = +27{\cdot}8°$ in chloroform. This substance has been named "hygrosterol" by the present authors. One acetyl, two bromo- and one chloro-derivatives as also a digitonide of the substance have been prepared and described in the Experimental; the carbanilate and the benzoyl derivatives were unsuccessful.

Besides the above mentioned hygrosterol, the roots of *H. spinosa* on further examination, yielded a trace of an essential oil, a yellowish-green wax, a sticky gum and a comparatively large quantity of maltose. The ash obtained from the roots on ignition was found to consist mostly of potassium salts.

Experimental.

The fresh roots of *Hygrophyla spinosa* procured locally were washed free from mud and dirt, cut up into small pieces by means of a chopping machine, sun-dried and extracted in 50 gram-lots by various solvents in a Soxhlet's apparatus. The solvent was subsequently evaporated. A preliminary examination of the root by the

usual methods indicated the presence of an enzyme in traces and absence of alkaloids.

Petroleum ether extract (1·05%).—Pale greenish-yellow oil containing a few colourless needle-shaped crystals. The amount of the latter was too small to be isolated, but from the appearance it seemed to be hygrosterol.

Carbon tetrachloride extract (1·2%).—Greenish-white substance having a waxy consistency and greasy feel. The product on repeated crystallisation from alcohol was obtained in the from of needle-shaped, radiating clusters which were still soft and greasy to the touch and melted indefinitely between 50° and 90°. It gave the colour reactions of hygrosterol, but apparently was in an impure condition.

Benzene extract (1·4%).—Soft greenish-white wax with properties similar to the above.

Chloroform extract (1·65%).—Pale green wax admixed with a trace of an yellow oil. Properties similar to the above. The green colour was due to the presence of traces of chlorophyll.

Carbon disulphide extract (1·73%).—Pale green wax with properties similar to the above.

Acetone extract (2·2%).—Dark brown sticky substance with a powerful aromatic odour. Fehling's solution was rapidly reduced and on distillation in steam it yielded a trace of volatile oil. Apparently the substance was contaminated with sugar.

Alcoholic extract (4·8%).—Pale green sticky wax, reducing Fehling's solution rather rapidly. On examination it was found to contain 1·7% of reducing and 2·4% of total sugars estimated as glucose. This was the extract which gave the largest yield of hygrosterol, and consequently the operation was repeated on a large scale.

3 Kg. of the dried and chopped roots were extracted with 6 litres of rectified spirit in a large extraction apparatus by boiling for eight hours. The extract was allowed to stand at the ordinary temperature for 24 hours, when a large quantity of a brownish-white precipitate collected at the bottom. The clear supernatant liquid was siphoned off and the precipitate filtered and washed with a little absolute alcohol. It was first dried in a steam-oven and then in a vacuum desiccator. The substance (88 g.) was purified by repeated crystallisation from 80% alcohol with the addition of animal charcoal and finally obtained as fine, colourless, stout prisms melting between

100° and 110° with charring and decomposition. The osazone which was prepared by the usual method melted at 206° and was found to be identical with maltosazone. Thus the substance was maltose.

The acoholic mother-liquor from the above substance was distilled from a water-bath until alcohol ceased to come over. The syrupy product on distillation in steam yielded an opalescent distillate from which ether extracted a trace of a pale yellow oil with a peculiar aromatic odour. The quantity however was too insufficient for any systematic examination.

The residue after steam distillation was filtered and washed several times with hot water. The filtrate was greenish-yellow in colour, slightly acid towards litmus and reduced Fehling's solution very readily. It contained a fair amount of reducing sugars, mainly glucose and maltose.

The residue from the above operation (29 g.) on drying, was found to be contaminated with an yellow oil, which could not be eliminated by spreading the substance on a porous plate. On extraction with petroleum ether the product was divided into two fractions, namely, a major fraction (17 g.) which was a colourless crystalline solid having only a slightly sticky feel, and a minor fraction (12 g.) which was an exceedingly sticky greenish-yellow wax. The crystalline solid was recrystallised several times from dilute alcohol with the addition of animal charcoal and finally obtained in the form of colourless glistening needles melting at 194°. It gave all the characteristic colour reactions for phytosterol with concentrated sulphuric acid in presence of iodine, chloroform and acetic anhydride. It showed a rotation of $[\alpha]_D^{28} = +27{\cdot}8°$ in chloroform. (Found: C, 84·06; H, 11·6; M.W. (cryoscopic in benzene), 396. $C_{28}H_{46}O$ requires C, 84·42; H, 11·55 per cent.; M.W., 398).

The greenish-yellow wax mentioned above could not be induced to crystallise from any solvent under any condition. Under the microscope it was found to consist of colourless needles (resembling those of hygrosterol) embedded in a matrix of tenacious greenish-yellow wax which apparently prevented the isolation of the former. The substance was therfore refluxed on the water-bath with ten times its weight of saturated alcoholic potash for three hours, when it completely went into solution with a reddish-brown colour. The solution was diluted with an equal volume of hot water and the liquid allowed to cool, when a mass of colourless crystals separated out. These were filtered off and recrystallised from dilute alcohol

when colourless glistening needles, m. p. 194°, were obtained, and were found to be identical with hygrosterol already described. The alcoholic mother-liquor on large dilution with water became turbid with separation of minute yellow globules which could not be induced to solidify. The quantity also was too insufficient for further examination.

Acetylhygrosterol.—Hygrosterol (1·5 g.) was heated under reflux for one hour with an excess of acetic anhydride and fused sodium acetate. On pouring into water and stirring for some time, the acetyl derivative separated in colourless flocks which were collected and crystallised from dilute alcohol in small needle-shaped crystals melting at 208°. (Found : C, 81·52 ; H, 11·22. $C_{28}H_{45}O{\cdot}CO{\cdot}CH_3$ requires C, 81·81 ; H, 10·91 per cent.).

Hygrosterol Hydrobromide.—Hygrosterol contains a double linkage and so it readily adds on hydrogen bromide and bromine. The hydrogen bromide addition product was prepared by heating 0·8 g. of the substance with 3 c.c. of fuming hydrobromic acid in a tightly-closed Florence flask on the water-bath for six hours. After cooling the flask was carefully opened and the contents washed out with water and filtered. The crystalline residue was recrystallised from a mixture of alcohol and chloroform (3 : 1) and obtained in the form of yellowish-white microscopic needles melting at 59°. (Found : Br, 16·32. $C_{28}H_{47}OBr$ requires Br, 16·66 per cent.).

Dibromohygrosterol dibromide.—Hygrosterol (1·4 g.) dissolved in 30 c.c. of chloroform was treated with a chloroform solution of bromine, until the latter was in excess. On allowing the mixture to stand for about 12 hours, the original dark red colour of the solution faded to pale yellow and hydrobromic acid fumes were envolved. The excess of bromine and the solvent were driven away from the mixture by passing a rapid current of air, and the sticky yellow solid crystallised from a mixture of alcohol and chloroform in the form of yellow microscopic needles, m. p. 138—139° (yield, 1·3 g.). (Found: Br, 44·81. $C_{28}H_{44}OBr_4$ requires Br, 44·66 per cent.).

Action of Thionyl Chloride on Hygrosterol.—Hygrosterol (0·8 g.) and thionyl chloride (2 c.c.) were heated on the water-bath for one hour. On allowing it to stand for about 12 hours, the reaction product completely solidified. It was then crystallised a number of times from a mixture of alcohol and chloroform (3 : 1) and finally obtained in the form of yellowish-brown prism melting at 101-103°. Besides chlorine, the substance was found to contain sulphur as well

which could not be eliminated under any conditions. Consequently it was not analysed.

Hygrosterol-digitonide.—This was prepared according to the method of Windaus (*Ber.*, 1909, **42**, 240) by mixing a hot solution of 1 g. of digitonin in 100 c.c. of 90% alcohol with a solution of 0·4 g. of hygrosterol in 60 c.c. of 95% alcohol. As nothing separated on allowing the mixture to stand, the solution was evaporated to about half its bulk and cooled when a quantity of fine white needles separated out. These were filtered, washed with 80% alcohol and dried at 120°. The substance had no definite melting point, but it decomposed between 220° and 230°. (Found: C, 61·42 ; H, 9·39. $C_{28}H_{46}O \cdot C_{55}H_{94}O_{28}$ requires C, 62·25 ; H, 8·75 per cent.).

One of us (N.N.G.) wishes to express his indebtedness to the Kanta Prasad Research Trust of the Allahabad University for a scholarship which enabled him to take part in the investigation.

CHEMICAL LABORATORY,
ALLAHABAD UNIVERSITY.

Received January 12, 1931.

Mercury Acetamide as a Mercurating Agent.

By K. G. Naik and L. D. Shah.

The mercuration of organic compounds has been studied by a number of workers (Dimorth, *Ber.*, 1898, **31**, 2154 ; 1899, **32**, 758 ; 1902, **35**, 2044 ; Schoeller and Scrauth, *Ber.*, 1908, **41**, 2089 ; 1909, **42**, 778 ; Hoffmann, *Ber.*, 1898, **31**, 1904 ; 1900, **33**, 1328 ; Petterson, *J. pr. Chem.*, 1912, **86**, 458, etc.). The most commonly employed reagents are mercuric oxide and the acetate but mercury acetamide has seldom been used for the purpose. The only isolated instance where mercury acetamide is used as a mercurating agent is its action on methyl methylmalonate (Schoeller and Scrauth *Ber.*, 1909, **42**, 784).

From the experiments recorded herein, it appears that mercury acetamide can be employed as fruitfully as the acetate for the preparation of organomercury compounds. Thus the substances enumerated below, *viz.*, (1) cyanacet-methylamide, (2) cyanacet-ethylamide, (3) cyanacet-propylamide, (4) cynacet-butylamide, (5) cyanacet-*iso*butylamide, (6) cynacet-amylamide, (7) cynacet-*iso*hexylamide, (8) cyanacet-heptylamide, (9) ethyl cyanoacetate, (10) cyanoacetamide, (11) cyanoacetanilide, (12) cyanacet-*m*-toluidide, (13) cyanacet-*o*-toluidide, (14) cyanacet-*p*-toluidide, (15) cyanacet-benzylamide, (16) cyanacet-α-naphthylamide, (17) cyanacet-β-naphthylamide, (18) cyanacet-1:3:4-xylidide, (19) cyanacet-1:4:5-xylidide are all attacked by mercury acetamide, one of the hydrogens of the reactive methylene group being replaced by the hydroxymercuri (—HgOH) group.

The properties of the compounds indicate the presence of a very weak C—Hg bond such as is always found when the carbon involved is in the α-position to a -CO-group. Thus they are readily decomposed by hot 0·25*N*-hydrochloric acid. Hydrogen sulphide, ammonium sulphide or sodium sulphide causes the formation of black mercuric sulphide. Potassium iodide ruptures the C—Hg linkage with the consequent formation of alkali hydroxide. Phenylhydrazine and hydrazine hydrate are found to liberate metallic mercury.

The general constitution assigned to the above compounds follows from the considerations given below:—

1. That the mercury atom has not replaced the hydrogen atom of the aromatic nucleus because—

(*a*) Cynacet-methylamide which does not contain such a nucleus forms a similar hydroxymercuri-derivative.

(*b*) A study of the known mercury compounds shows that the nuclear mercury atom is not decomposed by dilute hydrochloric acid (0·25*N*) (*cf.* Scrauth and Baurschmidt, *Ber.*, 1914, **47**, 2740), whereas hydroxymercuricyanacetanilide is decomposed by hot 0·25*N*-hydrochloric acid.

2. That the mercury atom has not replaced the hydrogen attached to the nitrogen atom of the —NHR group, for—

(*a*) Ethyl cyanoacetate, which does not contain such a hydrogen, forms a similar mono-mercurated product with mercury acetamide.

(*b*) The properties of the compounds suggest a carbon-mercury rather than a nitrogen-mercury linkage, because, whereas all the N—Hg compounds are decomposed by *cold* dilute acid (*cf.* Ley and Kissel, *Ber.*, 1899, **32**, 1357) the compounds described herein are decomposed by *hot* dilute acids only.

3. That the mercury atom has not entered the aliphatic part of the amido-group, because—

(*a*) Cyanoacetamide which does not contain such an aliphatic part forms a similar hydroxymercuri-compound.

4. That the mercury atom is directly attached to the carbon atom of the methylene group, for—

(*a*) Hydroxymercuricyanacet-benzylamide gives monobromocyanacet-benzylamide on treatement with bromine in aqueous suspension.

(*b*) The properties and behaviour of the compounds obtained herein exactly correspond with those having mercury in the α-position to a keto or a phenyl group which renders the α-mercury atom unusually reactive.

Cyanoacetamide reacts with mercury acetamide in aqueous or alcoholic solution giving hydroxymercuricyanoacetamide, which is formulated as $CN{\cdot}CH(HgOH){\cdot}CO{\cdot}NH_2$. This constitution has been assigned to the compound on the ground that on treatment with bromine in aqueous suspension it gives dibromocyanoacetamide which

is identical with the one obtained by Hesse (*J. Amer. Chem. Soc.*, 1896, **18**, 735) by the direct bromination of cyanoacetamide.

Petterson (*J. pr. Chem.*, 1912, *ii*, **86**, 458) obtained from mercuric acetate and ethyl cyanoacetate, hydroxymercuricyanoacetic ester, $CN{\cdot}CH(HgOH){\cdot}CO_2Et$. Probably an acetoxy-mercury derivative is first formed which subsequently undergoes hydrolysis under the experimental conditions. Mercury acetamide also reacts with ethyl cyanoacetate giving a quantitative yield of the hydroxymercuri-derivative. In all probability an acetamido-derivative is first formed which then undergoes hydrolysis as represented below:—

$$CN{\cdot}CH_2{\cdot}CO_2Et \xrightarrow{Hg(NHAc)_2} CN{\cdot}CH(Hg{\cdot}NHAc){\cdot}CO_2Et \xrightarrow{H_2O} CN{\cdot}CH(HgOH){\cdot}CO_2Et.$$

The formation of the same product from mercuric acetate and mercury acetamide naturally raises the question as to the constitution of the latter. Ley and Kissel (*Ber.*, 1899, **32**, 1857) deduced from the low electrical conductivity of mercury acetamide that it contains an N—Hg bond. It is well-known that, in order that a mercuric salt may react with an aromatic organic compound it must be capable of hydrolytic dissociation. Hence it may be that during the reaction between mercury acetamide and substituted cyanoacetamides, the former may react in the tautomeric form (II) containing the O—Hg linkage.

$$\underset{\text{(I)}}{(CH_3{\cdot}CO{\cdot}NH)_2Hg} \rightleftarrows \underset{\text{(II)}}{(CH_3{\cdot}C(NH){\cdot}O)_2Hg}$$

The latter form is susceptible to hydrolytic dissociation, since all mercuric salts of oxyacids are considerably hydrolysed in aqueous solution.

Experimental.

The hydroxymercuri-derivatives of the substituted cyanoacetamides were prepared by the action of mercury acetamide on the cyanoacetamides in equimolecular proportion in presence of alcohol.

Hydroxymercuricyanacetmethylamide.—Cyanacetmethylamide (2 g.) dissolved in alcohol, was heated to boiling and a hot solution of mercury acetamide (6·5 g.) in alcohol was added. A snow white flocculent precipitate immediately appeared which settled down in the course of about twelve hours. The precipitate was washed with alcohol and then with distilled water several times in order to remove any unchanged reactants. The product is insoluble in most organic solvents. It begins to turn brown at 287° but does not melt till 300°. (Found: Hg, 63·98 ; N, 8·74. $C_4H_6O_2N_2Hg$ requires Hg, 63·69 ; N, 8·90 per cent.).

Action of Potassium Iodide.—0·127 G. of the above compound was suspended in water and about one g. of potassium iodide was added. The mixture was refluxed on a sand-bath for four hours and the liberated alkali was titrated against 0·0174*N*-hydrochloric acid of which 44·7 c.c. were required. This shows the presence of 1·923 equivalents of alkali indicating that the splitting of the C—Hg linkage is almost quantitative.

Action of Hydrochloric Acid.—The above mercury compound is slowly decomposed by 0·25*N*-hydrochloric acid (hot) giving the original amide and mercuric chloride.

Action of Phenylhydrazine.—About 1 g. of the mercury compound was treated with 2 c.c. of phenylhydrazine. A vigorous reaction ensued in the cold and effervescence due to liberated nitrogen was observed. A grey precipitate of metallic mercury was formed which quickly collected and settled at the bottom of the flask. The mixture was then diluted with water and filtered. The solution on concentration and cooling deposited shining needles of pure cyanacetmethylamide, m.p. 101°.

Hydroxymercuricyanacetethylamide.—This was prepared from 1 g. of cyanacetethylamide and 2·9 g. of mercury acetamide. It does not melt till 300° but turns brown above 285°. (Found: Hg, 60·70 ; N, 8·76. $C_5H_8O_2N_2Hg$ requires Hg, 60·98 ; N, 8·54 per cent.).

*Hydroxymercuricyanacet-*n*-propylamide* was prepared from equimolecular quantities of cyanacet-*n*-propylamide and mercury acetamide in presence of alcohol. It begins to turn brown above 265° and melts with decomposition at 280°. (Found: Hg, 58·24; N, 8·42. $C_6H_{10}O_2N_2Hg$ requires Hg, 58·48; N, 8·19 per cent.).

*Preparation of Cyanacet-*n*-butylamide.*—In the preparation of the alkyl amides of cyanacetic ester the method of Bakes, West and Whitely (*J. Chem. Soc.*, 1921, **119**. 367) was employed, Ethyl

cyanoacetate (10 g.) and *n*-butylamine (6·5 g.) were mixed up in a sealed tube which was kept for twenty-four hours and then heated at 125° for six hours. After cooling the red crystalline mass was washed with petroleum and crystallised from benzene—petroleum mixture when it separated in the form of white slender needles, m.p. 73°. It is very soluble in alcohol, chloroform, benzene, and toluene but sparingly in petroleum. (Found: N, 20·26. $C_7H_{12}ON_2$ requires N, 20·00 per cent.).

Hydroxymercuricyanacet-n-*butylamide*.—Prepared from cyanacet-*n*-butylamide and mercury acetamide in the usual manner, it did not undergo any change till 300°. (Found: Hg, 55·88 ; N, 8·12. $C_7H_{12}O_2N_2Hg$ requires Hg, 56·18 ; N, 7·87 per cent.).

*Preparation of Cyanacetiso*butylamide.—Ethyl cyanoacetate (10g.) and *iso*butylamine (6·5 g.) were condensed in the usual way. The mixture on strong cooling solidified. It was purified by crystallisation from hot water (charcoal). It is very soluble in all the organic solvents, and melts at 45°. (Found: N, 20·06. $C_7H_{12}ON_2$ requires N, 20·00 per cent.).

*Hydroxymercuricyanacetiso*butylamide turns brown above 280° but does not melt till 300°. (Found: Hg, 56·43; N, 7·72. $C_7H_{12}O_2N_2Hg$ requires Hg, 56·18 ; N, 7·87 per cent.).

Preparation of Cyanacet-n-*amylamide*.—Ethyl cyanoacetate and *n*-amylamine were condensed in the usual manner. The product was crystallised from benzene—petroleum mixture after purifying it with bone charcoal. It formed feathery needles, m.p. 47°. (Found: N, 18·00. $C_8H_{14}ON_2$ requires N, 18·18 per cent.).

Hydroxymercuricyanacet-n-*amylamide* melts with decomposition at 285°. (Found: Hg, 54·40 ; N, 7·43. $C_8H_{14}O_2N_2Hg$ requires Hg, 54·06 ; N, 7·57 per cent.).

*Preparation of Cyanacetiso*hexylamide.—Ethyl cyanoacetate (10 g.) and *iso*hexylamine (9 g.) were condensed in the usual manner. The product is very soluble in alcohol, benzene, etc. It was crystallised from water as slender, colourless needles, m.p. 42°. (Found: N, 16·92. $C_9H_{16}ON_2$ requires N, 16·66 per cent.).

*Hydroxymercuricyanacetiso*hexylamide melts with decomposition at 273°. (Found: Hg, 51·96 ; N, 7·08. $C_9H_{16}O_2N_2Hg$ requires Hg, 52·09 ; N, 7·29 per cent.).

Preparation of Cyanacet-n-*heptylamide*.—This was prepared from ethyl cyanoacetate (10 g.) and *n*-heptylamine (10 g.) in the usual manner. It is very soluble in alcohol, acetone, ethyl acetate, and

benzene and sparingly in ether and petroleum. It separates from benzene—petroleum mixture in the form of fine, colourless needles melting at 67°. (Found: N, 15·20. $C_{10}H_{18}ON_2$ requires N, 15·38 per cent.).

Hydroxymercuricyanacet-n-heptylamide was prepared as usual from cyanacet-*n*-heptylamide and mercury acetamide. It turns brown at 270° and melts at 284°. (Found: Hg, 49·81 ; N, 6·99. $C_{10}H_{18}O_2N_2Hg$ requires Hg, 50·25 ; N, 7·04 per cent.).

Ethyl Hydroxymercuricyanoacetate.—Ethyl cyanoacetate was treated with the calculated quantity of mercury acetamide in alcoholic solution. The product is insoluble in most of the ordinary organic solvents and does not suffer any any change till 300°. (Found: Hg, 61·08 ; N, 4·37. $C_5H_7O_3NHg$ requires Hg, 60·79 ; N, 4·25 per cent.).

Action of Potassium Iodide.—0·1484 G. of ethyl hydroxymercuricyanoacetate was suspended in water and about 1 g. of potassium iodide was added. The mixture was refluxed for four hours and the liberated alkali was titrated against 0·0174*N*-hydrochloric acid (50·9 c.c.). This shows the presence of 1·96 equivalents of alkali, indicating the complete rupture of the C—Hg linkage.

Hydroxymercuricyanoacetamide was prepared from equimolecular quantities of cyanoacetamide and mercury acetamide in aqueous solution. It does not melt till 300°. (Found: Hg, 66·24 ; N, 9·70. $C_3H_4O_2N_2Hg$ requires Hg, 66·66 ; N, 9·33 per cent.).

Action of Bromine.—Aqueous bromine was slowly added to a suspension of the above compound in water, till it was no longer absorbed. The flask was finally heated on a water-bath for about half an hour. The solution was evaporated to dryness and the residue was extracted with benzene. On cooling the benzene extract, small needles separated out which, on recrystallisation from alcohol melted at 126°. It is identical with dibromocyanoacetamide.

The mercury derivatives of the substituted cyanoacetamides containing aromatic nuclei were similarly prepared by mixing equimolecular quantities of the amides and mercury acetamide in hot alcoholic solution.

Hydroxymercuricyanacetanilide does not undergo any change till 300°. (Found: Hg, 53·48 ; N, 7·22. $C_9H_8O_2N_2Hg$ requires Hg, 53·19 ; N, 7·45 per cent.).

Action of Hydrochloric Acid.—The above compound was treated with 25 c.c. of 0·25*N*-hydrochloric acid. On heating, a clear solution was obtained which on cooling deposited small needles which

were collected and on purification proved to be cyanacetanilide, m. p. 199°.

Hydroxymercuricyanacet-m-*toluidide* does not undergo any change till 300°. (Found: Hg, 51·70 ; N, 7·23. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28 ; N, 7·18 per cent.).

Hydroxymercuricyanacet-o-*toluidide* does not melt below 300°. (Found: Hg, 50·94. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28 per cent.).

Hydroxymercuricyanacet-p-*toluidide* does not melt till 300°. (Found: Hg, 50·90. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28 per cent.)

Hydroxymercuricyanacetbenzylamide melts with decomposition at 293°. (Found: Hg, 55·98. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28 per cent.).

Action of Bromine.—The above compound was treated with bromine till it was no longer absorbed. The flask was heated on a water-bath for about 15 mins. when a clear solution was obtained. On cooling, the solution deposited light, white tufts, which after recrystallisation from benzene melted at 92°. (Found: Br, 31·44. $C_{10}H_{10}ON_2Br$ requires Br, 31·62 per cent.).

Reduction of the Bromo-derivative.—0·138 G. of the substance liberated iodine equivalent to 54·6 c.c. of 0·02*N*-sodium thiosulphate. (Found: Br, 31·65. Calc. Br(labile), 31·62 per cent.).

Hydroxymercuricyanacet-α-*naphthylamide* turns grey at 253° and melts with decomposition at 272°. (Found: Hg, 47·23. $C_{13}H_{10}O_2N_2Hg$ requires Hg, 46·95 per cent.).

Hydroxymercuricyanacet-β-*naphthylamide* melts with decomposition at 283°. (Found: Hg, 46·71. $C_{13}H_{10}O_2N_2Hg$ requires Hg, 46·95 per cent.).

Hydroxymercuricyanacet-1:3:4-*xylidide* does not melt till 300°. (Found : Hg, 50·00. $C_{11}H_{12}O_2N_2Hg$ requires Hg, 49·51 per cent.).

Hydroxymercuricyanacet-1:4:5-*xylidide* does not undergo any change till 300°. (Found: Hg, 49·87. $C_{11}H_{12}O_2N_2Hg$ requires Hg, 49·51 per cent.).

The authors take this opportunity to express their gratitude to the Government of his Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work.

CHEMISTRY DEPARTMENT, THE COLLEGE, BARODA. *Received December* 11, 1930.

Reactivity of Conjugated Systems. Part III. Condensation of $\alpha:\beta$-Unsaturated Esters with Cyanoacetamide.

By Chittaranjan Barat.

The present work deals with the reactivity of the ethylenic bond in the system R·CH=CH·CO·OEt and strictly speaking falls under the category of Part I of this series which deals with the reactivity of the corresponding double bond in the system R·CH=CH·CO·R'. (Barat, *J. Indian Chem. Soc.*, 1930, **7**, 821). The following reasons, however, sufficiently justify its treatment in a separate paper, namely,

(1) the products obtained with the present set of compounds are fundamentally different from those obtained from the former series, and

(2) there seems to be a marked difference in the activity of the above-mentioned double-bond in these two series, due, no doubt, to the replacement of the carbethoxy group $-CO\cdot OEt$ in place of the acyl group $-COR$ as present in the previous set of starting compounds.

It is well-known that in a system of the type $>C=CH\cdot X$ (where X is a so-called negative group, *e.g.* $-COR$, $-CO\cdot OEt$, $-CO\cdot NH_2$, etc.) or in other words, where an ethylenic bond exists in the $\alpha:\beta-$position to a negative group X, the activity of that double-bond towards additive reactions in particular, is greatly influenced by the nature of the group X, *i.e.*, the activity increases with an increase in the negative character of X and *vice versa*. It is quite natural to expect therefore that the replacement of the rather strongly negative grouping $-CO\cdot R$ by the less negative one $-CO\cdot OEt$, the activity of the double-bond in the α-position to it will be greatly impaired, and this anticipation has been borne out by facts. When, however, the carbethoxy group is replaced by a slightly more negative carbonamide group $-CO\cdot NH_2$, the reaction takes place more readily than in the previous case. Quite a parallel case has been recently cited by Basu (*J. Indian Chem. Soc.*, 1930, **7**, 481 ; *cf.* also Meyer, *Ber.*, 1912, **45**, 2848).

The products of condensation described in the present work, belong to the glutarimide type. Such compounds do not appear to have been prepared by the present method, and advantage has been taken of this reaction to attempt the synthesis of 2:6-dihydroxy-pyridines, by dehydrogenating these compounds.

Although several methods of condensing these esters with acetoacetic, malonic and cyanoacetic esters are placed on record (Auwers, *Ber.*, 1891, **24**, 308 ; Auwers and Köbner, *ibid*, p. 1929 ; Auwers, Köbner and Meyenburg, *ibid*, p. 2888; Perkin and Thorpe, *J. Chem. Soc.*, 1899, **75**, 49 ; Thorpe, *ibid*, 1900, **77**, 923.; also Ingold and others, *ibid*. 1926, **128**, 1868) no attempt has yet been made to condense them with cyanoacetamide, when, no doubt, the following reaction takes place—

$$\begin{matrix} R\cdot CH{=}CH\cdot CO\cdot OEt \\ + \\ CN\cdot CH_2{-}CO\cdot NH_2 \end{matrix} \rightarrow \left[\begin{matrix} R\cdot CH-CH_2\cdot CO\cdot OEt \\ | \\ CN\cdot CH-CO\cdot NH_2 \end{matrix} \right]$$

(I)

$$\rightarrow \begin{matrix} R\cdot CH-CH_2\cdot CO \\ | \quad\quad | \\ CN\cdot CH-CO\cdot NH \end{matrix} \quad \ldots (1)$$

(II)

leading to the formation of a 2:6-diketo-3-cyano-4-(R)-piperidine. The other probability, namely that of the ester reacting as a ketonic ether is expressed as follows :—

$$\begin{matrix} R\cdot CH\cdot CH_2\cdot CO\cdot OEt \\ | \\ CN\cdot CH-CO\cdot NH_2 \end{matrix} \rightarrow \left[\begin{matrix} R\cdot CH\cdot CH_2\cdot C\cdot OEt \\ | \quad\quad \| \\ CN\cdot CH\cdot CO\cdot N \end{matrix} \right]$$

(I) (III)

$$\rightarrow \left[\begin{matrix} R\cdot CH\cdot CH{=}C \\ | \quad\quad \| \\ CN\cdot CH\cdot CO\cdot N \end{matrix} \right] \rightarrow \begin{matrix} R\cdot C{=}CH-CH \\ | \quad\quad \| \\ CN\cdot CH\cdot CO\cdot N \end{matrix} \quad \ldots (2)$$

(IV) (V)

But this latter scheme had to be discarded on the grounds that—

(1) the analytical figures of the condensation products correspond to a composition (II) and not to (V), and

(2) on hydrolysis the condensation products give rise to open-chain dibasic acids containing no nitrogen, which is only possible to compounds of type (II), whereas a compound (V) on hydrolysis would have given rise to 2-hydroxy-4-(R)-pyridines (*cf.* Barat, *loc. cit.*,

also *J. Indian Chem. Soc.*, 1930, 7, 851).

It is thus clearly established that the reaction takes place according to the scheme (1) ; the resulting products, belonging to glutarimide derivatives, suffer ring-fissure on hydrolysis and form β substituted glutaric acids (VII) possibly through the intermediary of an amido-acid (VI) as shown below.

$$\underset{\text{(II)}}{\begin{matrix} R\cdot CH-CH_2\cdot CO \\ | \quad\quad | \\ CN\cdot CH-CO\cdot NH \end{matrix}} \rightarrow \left[\begin{matrix} R\cdot CH-CH_2\cdot COOH \\ | \\ CN\cdot CH-CO\cdot NH_2 \end{matrix}\right]_{\text{(VI)}}$$

$$\rightarrow \underset{\text{(VII)}}{\begin{matrix} R\cdot CH-CH_2\cdot COOH \\ | \\ CH_2-COOH \end{matrix}} \quad \ldots (3)$$

The constitutions of these acids (VII) have been finally established by synthesising them from the appropriate aldehydes and ethyl malonate according to the method of Knoevenagel (*Ber.*, 1894, **27**, 2346).

Up till the present time it has not been possible to isolate compounds (I) and (VI) described above. The formation of (I) is precluded in a Michael's medium, where the elimination of alcohol is extremely easy. It would, however, have been possible to obtain it by Knoevenagel's method, but unfortunately these esters did not enter into combination with cyanoacetamide in the presence of Knoevenagel's reagent under ordinary circumstances. On the other hand, the free existence of a compound (VI) is rendered improbable between the two extreme tendencies of formation of the compounds (II) and (VII).

The amides of the corresponding acids have been condensed with ethyl cyanoacetate when products identical with (II) have been obtained according to the scheme—

$$\begin{matrix} R\cdot CH=CH-CO\cdot NH_2 \\ + \\ CN\cdot CH_2-CO\cdot OEt \end{matrix} \rightarrow \underset{\text{(II)}}{\begin{matrix} R\cdot CH-CH_2\cdot CO \\ | \quad\quad | \\ CN\cdot CH\cdot CO-NH \end{matrix}} \quad \ldots (4)$$

This reaction affords a further confirmation of the structure as given to these compounds. The reaction takes place with greater ease than with the esters of the corresponding acids and this further strengthens the theory that the more negative nature of the

$-CO\cdot NH_2$ group (than $-CO\cdot OEt$) enhances the reactivity of the double-bond in the α-position to it towards additive reactions.

Attempts are in progress to convert these compounds into 2;6-dihydroxypyridines by oxidation.

Experimental.

General Procedure.

As has already been indicated in the theoretical part, the condensation failed to take place by Knoevenagel's method and recourse had therefore to be taken to Michael's reaction alone to effect the condensations. To the usual suspension of sodiocyanoacetamide in absolute alcohol, the equivalent quantity of the ester was added, the mixture well shaken from time to time and left over till the odour of the ester completely disappeared. During this process of condensation the mixture usually developed a characteristic coloration which disappeared on the final acidulation of the mixture. The reaction was usually over in 3 or 4 days, but the isolation of the free condensation product was taken up usually after a week. The sodium salt was filtered off, washed with alcohol, dissolved in the minimum quantity of water, and acidulated with glacial acetic acid. The mixture was then cooled in ice, and the separated product filtered, washed with cold water, dried and crystallised. The cyanopiperidones that were thus formed were soluble both in alkalis and alkali carbonates, from which they were obtained unchanged on acidulation, excepting where it was also soluble in water. Their alcoholic or aqueous solutions did not give any coloration with ferric chloride, showing the absence of a hydroxyl group.

These compounds could be easily hydrolysed both by acids and alkalis but it was best achieved by means of 75% sulphuric acid as detailed in the previous works (*locc. cit.*). Where the dibasic acid formed did not separate on cooling and diluting the solution it was extracted by ether, and isolated by evaporation of the ethereal solution.

The dibasic acids so obtained were compared with identical specimens prepared by condensing the appropriate aldehyde with two molecular proportions of ethyl malonate according to the method of Knoevenagel (*loc. cit.*). The aldehyde and the ester were mixed together and left aside after the addition of a little piperidine. Next

day, the separation of a little water was observed and the mixture was heated under reflux for about half an hour; as the intermediate product (the tetra-carboxylic ester) was not required an equal volume of concentrated hydrochloric acid (*d*, 1.14) and another equal volume of water were added and the mixture heated under reflux till the evolution of carbon dioxide ceased. This usually took 6 to 8 hours, the mixture was then cooled, neutralised with sodium carbonate, the solution washed with ether (to remove any oily matter) and acidulated. The glutaric acid usually separated out, but was better extracted with ether, and the acid isolated therefrom. It was then purified by crystallisation and compared with the corresponding specimen.

Ethyl Acrylate and Cyanoacetamide.

The ester was prepared by the method of Münder and Tollens (*Annalen*, 1878, **167**, 222) and Caspary and Tollens (*ibid*, 248) from allyl alcohol. The yield was poor, on account of its tendency to polymerise and form a characteristic resinous matter on distillation (*cf.* Weger, *Annalen*, 1884, **221**, 80).

Formation of 2:6-Diketo-3-cyanopiperidine.—On mixing the components the mixture became blood red in colour, and shortly afterwards deposited a pink solid. After the usual time the mixture was carefully neutralised by dry hydrogen chloride, when the colour changed sharply into yellow; the sodium chloride was filtered off and the condensation product obtained by evaporation of the alcoholic solution (yield about 40%). It was soluble in almost all solvents (including water) excepting petroleum ether. Crystallised from alcohol it was obtained in short prisms, m.p. 206-7°. Its alcoholic solution turned violet on exposure to air, probably due to oxidation and consequent formation of the dihydroxypyridine which has been known to impart similar colorations (*cf.* Ruhemann, *J. Chem. Soc.*, 1898, **73**, 350). (Found: N, 20·10. $C_6H_6O_2N_2$ requires N, 20·29 per cent.).

Formation of Glutaric Acid.—The above compound was hydrolysed by sulphuric acid as usual, but the glutaric acid formed did not separate on cooling and diluting the solution. It was therefore extracted with ether, and isolated by evaporating the solvent. Crystallised from benzene it was obtained in colourless prisms, m.p. 97-98°. (Found: C, 45·24; H, 6·88; equiv. wt., 67·19. $C_5H_8O_4$ requires C, 45·45; H, 6·66 per cent.; equiv. wt., 66).

This was also synthesised from formaldehyde and ethyl malonate by Knoevenagel's method (*loc. cit.*). The purified product melted at 97-98°, and was identical with the specimen obtained above.

Ethyl Crotonate and Cyanoacetamide.

The ester was obtained according to the method of Michael (*Ber.*, 1900, **33**, 3766).

Formation of 2:6-Diketo-3-cyano-4-methylpiperidine.—Immediately on mixing the reactants the colour became reddish-violet and the sodium salt of the condensation product separated gradually. The free condensation product was separated as in the previous case, or by dissolving the sodium salt in the minimum quantity of water, neutralising the solution carefully with acetic acid, and cooling the solution with ice, when the product crystallised out. On crystallising from water it was obtained in colourless prismatic plates melting at 140-42°. It was very soluble in all solvents excepting petroleum ether and benzene (sparingly). (Found: N, 18·68. $C_7H_8O_2N_2$ requires N, 18·42 per cent.).

Formation of β-Methylglutaric Acid.—It was obtained by hydrolysing the above compound in an exactly similar way as in the previous case. It resembled its lower homologue in all its properties and crystallised from water in short prisms that melted at 85-86°. (Found: C, 49·58; H, 7·02; equiv. wt., 75·28. $C_6H_{10}O_4$ requires C, 49·31; H, 6·85 per cent.; equiv. wt., 73).

The acid could be directly obtained by treating acetaldehyde with ethyl malonate in alcoholic solution in presence of piperidine, and hydrolysing the product as before. It was found advisable however, to remove the alcohol before hydrolysis, as its presence appreciably hinders hydrolysis. The acid isolated as before and crystallised from water, melted at 85-86°, and was identical with the one obtained above.

Ethyl Cinnamate and Cyanoacetamide.

Formation of 2:6-Diketo-3-cyano-4-phenylpiperidine.—The reaction mixture exhibited a green coloration and the condensation took place more slowly than in the previous cases, as the odour of the ester was perceptible even after a week. But as the product

was insoluble in water it could be isolated with greater ease. (Yield about 65%.) Crystallised from alcohol, it was obtained in fine white scaly flakes melting at 224-25°, and but for its lesser solubility, resembled the other homologues in all its properties (Found: N, 13·38. $C_{12}H_{10}O_2N_2$ requires N, 13·08 per cent.).

The above compound was also obtained in a still better yield* (about 75%) when the amide of cinnamic acid, m.p. 145-47°, (prepared by the method of Autenrieth, *Ber.*, 1904, **34**, 184) was condensed in the usual way with ethyl cyanoacetate.

Formation of β-Phenylglutaric Acid.—When the above compound was hydrolysed by 75% sulphuric acid, and the reaction mixture diluted after being cooled, the acid separated as a thick oil which was extracted with ether. Crystallised from 40% alcohol it was obtained in fine white scales, m.p. 137-38°. (Found: C, 63·74; H, 6·01; equiv. wt., 108. $C_{11}H_{12}O_4$ requires C, 63·46; H, 5·77 per cent.; equiv. wt., 104).

The acid was directly obtained from benzaldehyde and ethyl malonate in the usual way. No solvent was employed, and the product melted at 137-38°, and was identical with the other specimen.

Ethyl p-*Nitrocinnamate and Cyanocetamide.*

Formation of 2:6-*Diketo*-3-*cyano*-4-p-*nitrophenylpiperidine.*—The condensation was carried out as usual and the condensation product separated as in the previous case. The product was almost insoluble in all solvents excepting glacial acetic acid and pyridine. Crystallised from either of these solvents it was obtained in yellow prisms, m.p. 279-80°. (Found: N, 16·51. $C_{12}H_9O_4N_3$ requires N, 16·22 per cent.) This compound was obtained in a far better yield when the amide of *p*-nitrocinnamic acid (m.p. 155°) was condensed with ethyl cyanoacetate ester as in the previous case.

Formation of β-p-Nitrophenylglutaric Acid.—The above compound was readily hydrolysed by 75% sulphuric acid, and the resulting acid easily separated on diluting the acid solution. The substance was fairly soluble in ether, alcohol, benzene and acetic acid, sparingly so

* This superiority in yield confirms the statement (*vide supra*) that the —CO·NH$_2$ group being more negative than the—CO·OEt group enhances the reactivity of the α : β-double bond.

in water and insoluble in petroleum ether. It crystallised in very pale yellow prismatic needles m. p. 238-40°. (Found: N, 5·36; equiv. wt., 128·05. $C_{11}H_{11}O_6N$ requires N, 5·62 per cent., equiv. wt., 126·5).

The acid was directly obtained from *p*-nitrobenzaldehyde and ethyl malonate in the usual way. The acid separated on diluting the hydrochloric acid solution and was filtered off, washed and crystallised from alcohol. It had m.p. 238-40° and was identical with the previously obtained sample.

The author is greatly indebted to Dr. H. K. Sen for his keen interest in the present investigation, and expresses his thanks to the Indian Chemical Society for a grant which has partly defrayed the cost of a few chemicals used in the course of the present work.

Department of Applied Chemistry,
University College of Science and Technology,
Calcutta.

Received December 20, 1930.

The Formation of the Sodium Derivatives of Compounds Containing a Reactive Methylene Group.

By K. G. Naik and L. D. Shah.

It is well-known that the hydrogen atoms in groupings such as

$$-CO-CH_2-CO- \qquad \equiv C-CH_2-C \equiv \qquad -CO-NH-CO-$$

$$H\cdot C \equiv \qquad HO\cdot C =$$

are replaceable by sodium, and that the property depends upon the accumulation of residual affinity in the immediate neighbourhood of the replaceable hydrogen. Bland and Thrope (*J. Chem. Soc.*, 1912, **101**, 874) have advocated that the stability of the sodium compounds of the various glutaconic esters must be dependent upon the acid character of the displaced hydrogen, the acidity being determined by the nature of the groups attached to the carbon atom which carries the hydrogen atom and they further hold that in those cases in which one carbethoxy group is attached to the carbon atom, the sodium compound is completely dissociated by water. It is also known that ethyl cyanoacetate and cyanoacetamide give mono-sodium derivatives (Henry, *Compt. rend.*, 1887, **104**, 1619; Hesse, *Amer. Chem. J.*, 1896, **18**, 724). The present work was therefore undertaken to study the relationship which may exist between the acid character of the hydrogen atom of a reactive methylene group and the formation of its sodium derivative by the replacement of such a hydrogen. The following substances were examined:

(1) Cyanacet-*m*-toluidide, (2) cyanacet-*o*-toluidide, (3) cyanacet-*p*-toluidide, (4) cyanacetbenzylamide, (5) cyanacet-α-naphthylamide, (6) cyanacet-β-naphthylamide, (7) cyanacetmethylamide, (8) cyanacetbutylamide and (9) cyanacetheptylamide.

All the substances enumerated above react with metallic sodium in presence of dry benzene or anhydrous ether, yielding products having the general formula, $CN\cdot CHNa\cdot COR$ (R=OEt, NH_2, NHMe, etc.),

The above general constitution has been assigned to the compounds from the following considerations:

(1) That the sodium atom has not replaced the hydrogen atom of the nucleus, for, cyanacetmethylamide which does not contain such a nucleus forms a similar mono-sodium derivative.

(2) That the sodium atom has not entered the aliphatic part of the amido group, for, cyanoacetamide which does not contain such an aliphatic part, forms a similar mono-substitution product with metallic sodium (Hesse, *loc. cit.*).

(3) That the sodium atom has not replaced the hydrogen attached to the nitrogen atom of the $-NH\cdot R$ group for,

(*a*) Ethyl cyanoacetate, which does not contain such a hydrogen forms a similar mono-substituted product with metallic sodium (Henry, *loc. cit.*).

Sidgwick and Brewer (*J. Chem. Soc.*, 1925, **127**, 2379) have shown that the alkaline derivatives of β-diketones, β-ketonic esters, *o*-hydroxy aromatic esters and aldehydes and *o*-nitrophenols behave in one of the three ways as exemplified below:

(I) The sodium derivative of ethyl malonate is insoluble in benzene and chars without melting: it behaves as a salt.

(II) The sodium derivative of ethyl methylmalonate dissolves in benzene to form a clear solution from which the compound does not separate immediately even on concentration; but once it has separated, it is quite insoluble in benzene or toluene.

(III) The sodium derivative of ethyl acetoacetate is soluble in hot toluene and melts to a clear liquid at 108°.

The compounds obtained during the present course of the work must be classed as salts of type I given above, since they are insoluble in benzene and toluene and do not give definite melting points.

During the course of their investigations on the factors governing the reactivity of the hydrogen atoms of a reactive methylene group situated between two negative groups as in the case of compounds containing the groupings

$$-CO\cdot CH_2\cdot CO- \quad \text{and} \quad CN\cdot CH_2\cdot CO-,$$

it has been observed by Naik and his collaborators (*J. Chem. Soc.*, 1921, **119**, 379; 1922, **121**, 2592, etc.) that the reactivity increases in direct proportion to the increase in the negativity of the carbonyl group with its attached groupings; so that in a series like—

(1) $CH_2(CO\cdot NH_2)_2$ (2) $NH_2\cdot CO\cdot CH_2\cdot CO\cdot NHR$

melted with decomposition at 200°. (Found: Na, 14·08; N, 17·37. $C_7H_{11}ON_2Na$ requires Na, 14·20; N, 17·28 per cent.).

Sodiocyanacetheptylamide.—This was prepared as in the preceding cases by the action of metallic sodium on cyanacetheptylamide in presence of anhydrous ether. A red solid was obtained which was repeatedly extracted with hot benzene and finally washed with light petroleum. It melted with decomposition at 195°. (Found: Na, 11·39. $C_{10}H_{17}ON_2Na$ requires Na, 11·27 per cent.).

The authors desire to express their gratitude to His Highness the Maharaja Gaekwar's Government for a grant by which the expenses incurred in this research were met.

CHEMISTRY DEPARTMENT,
THE COLLEGE, BARODA.

Received January 12, 1930.

A Modification of Pervier and Gortner's Method for the Estimation of Pentosans in Plant Tissues.

By R. C. Malhotra.

The physiological importance of pentosans in enabling a plant to survive severe temperature conditions has recently been recognised. The writer's work showed a need for testing out some of the accepted methods, at present used in American laboratories.

Pentosans are generally estimated by one of the two methods, namely, biological and chemical, whose detailed procedure is being recorded hereinafter. The former is based on the assumption that pentosans are not fermented by yeasts, and the latter on the conversion of pentosans into furfural by hydrochloric or sulphuric acid.

Spoehr (*Carnegie Inst. Pub.*, 1919, No. 287, p. 36) emphasises that fermentation is the most reliable method in the quantitative estimation of pentosans.

Salkowski (*Z. physiol. Chem.*, 1900, **30**, 478; 1902, **34**, 162), Cremer (*Z. Biol.*, 1892, **29**, 484), Neuberg and Wohlegemuth (*Z. physiol. Chem.*, 1902, **36**, 31), Frankland and MacGregor (*Ber.*, 1892, **25**, 800), Behrens (*Centr. Bact.*, 1898, **2**, 547), Peterson, Fred and Schmidt (*J. Biochem.*, 1922, **54**, 19; *J. Biol. Chem.*, 1924, **60**, 627), Tollen and others (*Annalen*, 1888, **249**, 257), Hawkins (*Amer. J. Bot.*, 1915, **2**, 375) and many other workers have shown the utilization of various organisms under varied conditions in such an estimation. Recently Rosa (*Missouri Ag. Exp. Sta. Res. Bull.*, 1921, No. 48) used Fleischmann's yeast for this purpose.

On the other hand, many chemists, such as Haas and Hill ("Chemistry of Plant Products"), Plimmer ("Practical Bio and Organic Chemistry"), Bokorny (*Chem. Abs.*, 1917, **11**, 2813), Englis and Hale (*J. Amer. Chem. Soc.*, 1925, **47**, 446), Conrad (*Missouri Ag. Exp. Sta. Res. Bull.*, 1926, No. 85), Bartholomew and Robbins (*Amer. J. Bot.*, 1926, **13**, 342), Davis and Sawyer (*J. Ag.*

Sci., 1914, **6**, 406), and Abbott (*Missouri Ag. Exp. Sta. Res. Bull.*, 1926, No. 85) question the advisability of the fermentation methods.

The chemical methods depend upon the conversion of pentoses into furfural by the action of sulphuric or hydrochloric acid. The sulphuric acid method with the modification that hydrazone be precipitated in the presence of sodium chloride (a tedious process) was recommended by the United States Department of Agriculture. However, Ling and Nanji (*Biochem. J.*, 1921, **15**, 466) tried to overcome this inconvenience by displacing the gasometric method by the iodometric one. The writer's experience shows that even this method is not very reliable. These authors used an extract of a few Indian grasses only. The writer has obtained some data (to be published shortly), which indicate that a fair percentage of pentosans cannot be extracted. Link (*J. Amer. Chem. Soc.*, 1929, **51**, 2506) has also shown that xylan is mixed up with cellulose of the cell wall.

Pervier and Gortner (*J. Ind. Eng. Chem.*, 1923, **15**, 1167) found that in the official method ("*Assoc. Official Agri. Chemists,*" 1920, p. 96) the reaction took place in 18 to 20 per cent. instead of 12 per cent. hydrochloric acid as is assumed, and that the acid of this concentration has destructive influence on furfural. They recommended the use of a slow current of steam through the distilling mixture to carry away the furfural as rapidly as it is formed. Its destruction by long contact with strong acid, however, has not been much avoided as they had expected. The delivery tube as used by them does not carry steam to all points alike, consequently, all parts of the mixture have not the same rate of reaction. Further they did not regulate the flow of steam.

Regarding the estimation of furfural in the distillate, one of the promising methods seems to be that of Powell and Whittaker (*J. Soc. Chem. Ind.*, 1924, **43**, 35T). Recently Deshpande (*J. Indian Inst. Sci., Bangalore*, Vol. 18A, Part 9) found Powell and Whittaker's method to be the most accurate.

Numerous other methods have been suggested, such as Jolles's (*Z. anal. Chem.*, 1906, **45**, 196) method of titration with sodium bisulphite, titration with phenylhydrazine and with Fehling's solution and thiobarbituric acid method; but all these are open to serious errors (*Carnegie Inst. Wash. Pub.*, 1919, No. 287). Pervier and Gortner tried several new methods unsuccessfully.

Experimental.

Materials.—McIntosh and Winter banana apples and tomatoes were used. The apple twigs were collected from a very uniform plot at the New York Agricultural Experiment Station, Geneva, N. Y. The tomato seeds were obtained from Professor Yeager of North Dakota, Fargo, out of his pure bred stock. The plants were grown at a uniform temperature of 50° at the University of Chicago, Chicago, Illinois. Three-year old apple twigs and tomato without roots were used. They were cut into small pieces, dried at 100° for one hour to kill all the enzymes present as recommended by Murneek (*Proc. Amer. Soc. Hort. Sci.*, 1928, **125**, 338), dried for 26 hours at 75°, cooled in a desiccator, ground, pulverized in a Wiley mill until they passed through a sieve with 80 meshes per inch, and collected. From these samples about 3 g. of material (in triplicate) were used for each of the experiments, except in Rosa and Spoehr's methods, where 10 g. samples were used. Pure xylan, which was purified by Wheeler and Tollen's method (*Annalen*, 1889, **254**, 304), was tried first.

Methods: A.—For the official method the sample was heated with 100 c.c. of 12% hydrochloric acid at such a rate that 30 c.c. of the distillate passed over in 10 minutes. Thirty c.c. more of the acid were added and the process was repeated till 360 c.c. of the distillate were obtained. This was made up to 400 c.c. by adding 12% hydrochloric acid and the furfural estimated as phloroglucide in the usual manner.

B.—In Pervier and Gortner's method a slow current of steam was used, other conditions being the same as in A.

C.—In Ling and Nanji's method, the outlines of these authors were followed, except that instead of 10 c.c. of $N/10$-iodine solutions, 20 c.c. were used. The excess of iodine was titrated against $N/20$-sodium thiosulphate.

D.—In Spoehr's method, the samples were heated with 1% hydrochloric acid under reflux for 3 hours, 40 c.c. of the acid being used for every 2 grams. The hydrolysed extract was divided into aliquots and adjusted to the desired hydrogen ion concentration with $N/10$-sodium hydroxide. Gillespie's (*Soil Sci.*, 1920, 9, 115) colorimetric method was used in determining the hydrogen ion concentration before and after sterilization and after fermentation. The reaction of the media was maintained at p_H 7·0 (neutral point).

To the sterilized neutral sample obtained, was added baker's yeast mixture, made to a thin paste by using 0·2 g. pressed yeast per g. of the original sample. Every time a fresh preparation of carefully washed baker's yeast was used, since it was realised that foreign substances in the yeast might cause an error. The vessel was stoppered with sterilized cotton and incubated for 40 hours at 35° as directed by Abbott (*loc. cit.*).

E.—In Rosa's method, Fleischmann's yeast cake was used. The solutions were not sterilized, but 8 per cent. alcohol was added before fermentation to prevent the growth of surface films, unless the fermentation was continued longer than 5 days.

In (D) and (E) the analyses were calculated in terms of c.c. of standardized Fehling's solution, reduced to one gram of fresh dry sample. The normality of copper sulphate solution used for making Fehling's solution was found by electrolytic method. The reducing value of the solutions was determined by heating with Fehling's solution, centrifuging and determining the copper sulphate left in an aliquot of the supernatant liquid by the method of Peters (*J. Amer. Chem. Soc.*, 1912, **34**, 928). Proper dextrose-copper factor as carefully determined by Peters and plotted by Abbott was used.

A suggested modified method.—An apparatus (Fig. 1) was set up.

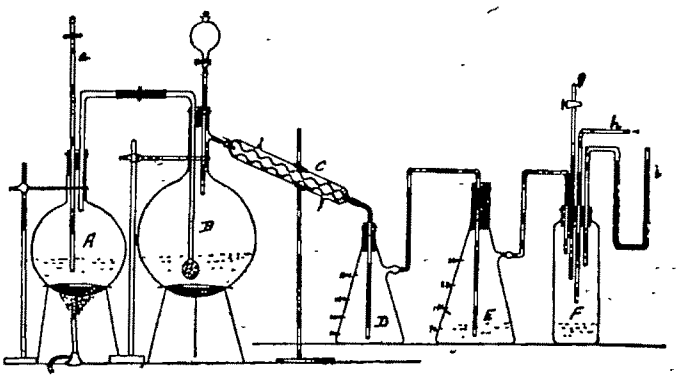


Fig. 1.

In flask *A* 100 c.c. of 3 per cent. hydrochloric acid was put through a separating funnel *a*. Flask *A* was connected with flask *B* by a perforated tube, which was placed in such a manner that a current of steam coming from the flask *A* would react equally with the contents of the flask *B*, which contained the sample, plus 100 c.c. of 9 per cent. hydrochloric acid. The stoppers were made

air tight with shellac. The distillate from condenser *C* was received in flasks *D* and *E*. The use of two catching flasks was necessary as a safety device against the back flow of the distillate. Flask *E* was connected with a suction bottle *F*, with which a safety device *g*, a tubing connecting suction pump *h* and a manometer *I* were attached. Both *h* and *g* could be used for reducing the suction pressure at will. Every precaution was taken to have all the connections air tight.

When the contents of flask *B* became hot, steam was released from flask *A* at such a rate that 100 c.c. of the distillate collected in flasks *D* and *E* per hour, more solutions were poured through the separating funnel maintaining the original volume. This was repeated until the distillate collected was 380 c.c. The discharge of the steam current was very slow. It could be regulated by means of a uniform but desired heat of the flame.

The steam current and the suction pressure formed a system having the least danger of the destruction of furfural. At no time hydrochloric acid was higher than 11%. The total pressure used was 15 cm. The subsequent operations were identical with those of the official method. This method gave very uniform results. The figures for pentosans were higher than any other existing chemical methods. As to the biological methods, as advocated by Spoehr and by Rosa, the results were so fluctuating, at least in the writer's experiments, that the data seemed to show a great unreliability of the use of these methods in the determination of pentosans. The results are being presented in Table I.

TABLE I.

Pentosan Content of Plant Tissues in Terms of Fresh Weight as Determined by Various Methods.

Tissue and lot.	Chemical methods.			Biological methods.		Pervier and Gortner's modified method.
	Official.	Pervier and Gortner's.	Ling and Nanji's.	Spoehr's.	Rosa's.	
I	II	III	IV	V	VI	VII
McIntosh apple						
A	5·810%	5·753%	6·031%	7·321%	6·173%	6·245%
B	5·372	5·981	6·328	2·834	3·533	6·292
C	5·526	6·012	5·812	4·951	2·827	6·331
Winter banana apple						
A	5·382	5·371	5·171	4·819	5·481	5·893
B	5·181	5·231	5·231	5 332	4·139	5·788
C	5·311	5·522	5·711	4·218	3·620	5·914
Tomato						
A	0·211	0·180	0·200	0·200	0·015	0·301
B	0·190	0·198	0·193	0·051	0·111	0·317
C	0·161	0·201	0·101	0·118	0·187	0·321
Pure pentosans (xylan)						
A	95·8	96·8	96·0	70·9	79·3	96·8
B	95·3	96·4	96·1	78·3	83·2	96 9
C	95·0	96·0	96·5	91·9	91·1	96·8

N.B.—Biological methods were again carried out in fives. Their general tendency seemed to be the same as indicated in Columns V and VI.

Discussion.

It will be seen from Column II, that the official method has given low and comparatively less uniform figures, which for pure pentosans are somewhat low also. Pervier and Gortner's method in the main (Column III) gave somewhat higher values than the official method, although they were not the highest. Furthermore, the percentages were not uniform. In case of pure pentosans figures agreed fairly well among themselves and reached near the maximum probable yield.

The main source of some error in Pervier and Gortner's method has already been pointed out. Absence of uniformity in this as well as in the official method may be attributed to the following factors: (*a*) some material adheres against the walls of the vessels. The tubing delivering steam cannot possibly react with this adherent material due to lack of perforation. (*b*) The incoming and the outgoing steam are not properly regulated. (*c*) There is still a higher concentration of hydrochloric acid with which the contents of the flask come in contact.

Figures by Ling and Nanji's method (Column IV) are not very constant. In some cases they are lower than those obtained by Pervier and Gortner's method, although, on the whole, they are higher than those in Columns II and III, except for the pure pentosans. The author thinks that this method (no matter how convenient it may appear) has the least satisfaction of all the chemical methods suggested, up to now, for the estimation of pentosans.

Of the biological methods (Columns V and VI) it seems that both Spoehr and Rosa's methods are unreliable, because they yield lower figures. In comparing these methods with any of the chemical methods, it may be noted that, in the main, chemical methods are more satisfactory, at least with these tissues. The writer agrees with those who have already noted the unreliability of fermentation methods. It seems to the writer that until we learn more about the specific nutrition of various organisms and the conditions under which combined carbon can be used by them, biological methods will remain unsafe in this type of problems.

According to the writer's method (Column VII) it seems, that on the whole, pentosan content is higher than any method. For instance, by the modified method, average figures of McIntosh apple indicate a difference of approximately 12·4% for the official, 8·0% for Pervier

and Gortner's, 5% for Ling and Nanji's, 21% for Spoehr's and 65% for Rosa's methods. All other averages are also high, although the figures for pure pentosans do not seem to show such a divergence. The analysis of pure pentosans by means of the different chemical methods with the exception of the official method, shows hardly any difference. It seems that the destruction of pentosans by these methods is in a small measure due to these reagents (except in the official method), but mainly due to the effect of foreign matters on pentosans. When there are substances other than pentosans, as found in a plant tissue, the reagents may induce the formation of stable non-volatile products with furfural, or the decomposition of furfural. It may be probable also, that the pentosans present in plant change into furfural and some other products, while pure pentosans give only furfural. More work has to be done before such conclusions can be warranted. No claim has been made to study the effect of methyl or hydroxymethyfurfural, pectic or uronic acids on the result.

Conclusions.

A modification of Pervier and Gortner's method for the pentosan determination has been proposed, which seems to yield higher and uniform results. Biological methods seem to have many sources of error and are therefore unreliable. No claim has been made that this method has any advantage over other chemical methods (except the official) for the pure pentosans.

It is a pleasure to thank Dr. Karl P. Link, Associate Professor of Agricultural Chemistry, University of Wisconsin, Madison, for a supply of xylan and to Miss Elvera Hanket of Northwestern University for going through the MS.

GRADUATE SCHOOL OF SCIENCE,
UNIVERSITY OF CHICAGO,
CHICAGO, ILLINOIS, U.S.A.

Received June 2, 1930.

Organo-antimony Compounds. Part V. Preparation of some Substituted Benzyl Benzoates and their Antimony Derivatives.

By Sudhir Chandra Niyogy.

In a recent paper, Gough and King (*J. Chem. Soc.*, 1930, p. 669) has discussed the relationship between the chemical constitution of a series of compounds starting from benzamide-*p*-arsinic acid and their trypanocidal activity, on *Trypanosoma equiperdum* in rats. The conclusions which the above authors have arrived at are very interesting. It has been demonstrated that benz-*m*- and -*p*-arsinic acids, hippuro-*p*-arsinic acid, salicylic acid-5-arsinic acid, *p*-sulphophenylarsinic acid, as also the corresponding arsinous acids, are inactive against experimental trypanosomiasis in mice, but when these are converted into their corresponding amides, trypanocidal activity appears in every case. The inactivity of the first series of arsenicals has been explained by assuming that so long as the compounds contain the free carboxyl or sulpho-group, they are capable of forming soluble salts and of being rapidly excreted from the system, whether the arsenic is present in the tri- or penta-valent condition. On the other hand, the amides are also excreted, though probably at a slower rate, so long as the arsinic acid group remains intact, and they are capable of forming soluble salts. When, however, the pentavalent arsinic acid has been reduced to the trivalent arsinous stage, they will no longer be capable of forming soluble salts, but they will then be liberated in the colloidal state and consequently will not be excreted rapidly. The conversion of pentavalent arsinic acids to the trivalent arsinous acids is supposed to take place through the action of thiol-derivatives, in tissues. The excess of thiol groups then combines with arsinous acids thus produced, forming arylthioarsinites (*cf.* Ehrlich, *Ber.*, 1909, **42**, 42; Voegtalin, *Physiol. Rev.*, 1925, **5**, 68). The continuous and gradual hydrolysis of the arylthioarsinites would lead to the production of small quantities of highly toxic arsinous acids and this process maintained for a considerable time would be responsible for the disappearance of the trypanosomes with resultant cure,

But there is one consideration which goes seriously against this elaborate theory of trypanocidal action. It has been observed in the routine test of arséno-compounds, that even after the first application of the drug in rats, infected with *Trypanosome equiperdum*, the number of tryponosomes per c.c. diminish very rapidly, within twenty-four hours. It is not possible to assume that the elaborate operations discussed above, would be complete within this short time and the theory of Gough and King cannot therefore be accepted as it stands. Another experimental fact which goes against this amide theory is the entire lack of activity of a number of stibinic acids prepared from benzyl *o*-, *m*-, and *p*-aminobenzoates (Niyogy, *J. Indian Chem. Soc.*, 1930, 7, 577). If it is assumed that the only influence of the amide group is to depress the tendency of formation of soluble salts, it is strange that these stibinic acids, in which the carboxyl group is protected by a benzyl group and in consequence, incapable of forming salts, should exhibit no trypanocidal activity. From this it must be admitted that amide formation not only prevents the formation of soluble salts but also brings about some fundamental difference in the nature of the compounds. The inefficiency of the stibinic acids mentioned above might be due, as suggested by Gough and King (*loc. cit.*) to any of the following causes: (*i*) the esterification of carboxyl group probably removes the stibinic acid from the range of the reduction potential of the tissues and thus they remain in the pentavalent form which is rapidly removed from the system; (*ii*) the ester may not combine so very easily with thiol complexes, as the amide; (*iii*) the hydrolysis of the arylthiostibinites may not proceed so easily as with amides.

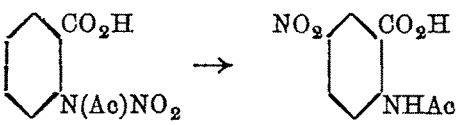
Among the antimonials which have been prepared thus far, it has been found that only the aminophenylstibinic acid and some of its derivatives are active against infections caused by Leishman-Donovan bodies. Of the three isomers, the *para*-compound has been studied more systematically than the others and appears to possess a therapeutic index sufficiently high to be employed in practice. Now according to the theory of trypanocidal activity put forward by Gough and King, the *para*-compound may fulfil the conditions laid down in the previous paragraph while the isomeric benzyl esters mentioned before do not conform to them and are consequently of no therapeutic value. Assuming, therefore, that for the production of an active trypanocide, an amino-group must be present in *para*-position to the stibinic acid residue, an attempt has been made to prepare benzyl

benzoate-2-aminophenyl-5-stibinic acid. The effect of elongating the acyl group which is employed for protecting the 2-amino-group was also considered to be of interest and has been one of the objects of the present communication. Moreover an attempt has also been made to prepare a compound of the type benzyl benzoate-2-acylamino-5-stibinic acid, so that the influence of the alkoxy group on the trypanocidal action, if any, may be studied further.

The starting materials are obviously 5-nitro-2-aminobenzoic acid and 5-nitro 2-aminobenzyl alcohol. In order to obtain both as the result of a single operation, the most suitable starting material is undoubtedly 5-nitro-2-acetylaminobenzaldehyde (Cohn and Springer, *Monatsh.*, 1908, **24**, 96). By the application of Cannizzaro's reaction 5-nitro-2-acetylaminobenzoic acid and 5-nitro-2-acetylaminobenzyl alcohol were expected ; but in practice, it was found that the acetyl group was knocked off in the course of the reaction and free amines were isolated. Both the acid and the alcohol were then re-acetylated with acetic anhydride.

The m.p. of 5-nitro-2-acetylaminobenzoic acid, prepared by the direct nitration of 2-acetylaminobenzoic acid, had been given by Rupe (*Ber.*, 1897, **30**, 1097) to be 152° while Ullmann and Uzbachian (*Ber.*, 1903, **36**, 1797) had obtained the same compound with m.p. 221°, by the oxidation of 5-nitro-2-acetylaminotoluene with calcium permanganate, the m.p. of the base, 5-nitro-2-aminobenzoic acid being 263°. In the present investigation the m.p. of 5-nitro-2-aminobenzoic acid prepared by Cannizzaro's reaction from the corresponding aldehyde was found to be 262-63° which on acetylation gave a product which melted at 216-17°. It would appear from these observations that the product obtained by Rupe (*loc. cit.*) was not the expected 5-nitro-compound. To settle this question, it was considered necessary to repeat the experiments of the previous authors. Careful repetition of Rupe's experiment showed that in some cases, the product had m.p. 152° while in a few cases, the m.p. was 217-18°. Although Ullmann and Uzbachian (*loc. cit.*) had worked with 5-nitro-2-acetylaminotoluene, yet no reference or details of its preparation had been given by the authors ; the literature (*Z. Chem.*, 1871, *ii*, **7**, 99) contains a single reference to this compound. For the purpose of the present work, *o*-acetotoluidide was nitrated in sulphuric acid solution and the product was then oxidised with potassium permanganate and magnesium sulphate (compare D.R.P. 94629) to give a nitroacetylaminobenzoic acid

which after purification had m.p. 216-17°. This m.p. was not depressed when this product was mixed with a sample of 5-nitro-2-acetylaminobenzoic acid, prepared from the corresponding aldehyde. This operation not only enables one to correct the m.p. of 5-nitro-2-acetylaminobenzoic acid but also to establish the constitution of the nitration product of 2-acetylaminotoluene. Thus it appears that the m.p. of 5-nitro-2-acetylaminobenzoic acid is 216-17° as described by Ullmann and Uzbachian (*loc. cit.*). The product of m.p. 152° obtained by Rupe might have been a nitro-amino-compound of the following type, the nitro group subsequently migrating to position 5.

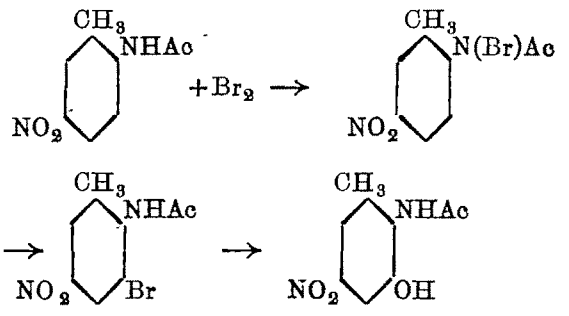


M.p. 152-53° M.p. 216-17°

But unfortunately when attempts were made to bring about this conversion by warming the product of m.p. 152°, with dilute mineral acids, the acetyl group was knocked off and 5-nitro-2-amino-benzoic acid, m. p. 262-63°, was obtained in every case.

The next step was the preparation of the required esters, benzyl 5-nitro-2-acetylaminobenzoate and 5-nitro-2-acetylaminobenzyl benzoate. All common methods failed to give the ester of 5-nitro-2-acetylaminobenzoic acid with benzyl alcohol. By converting the carboxylic acid into the silver salt and heating this in benzene suspension with benzyl chloride, the ester was obtained. But up till now, all attempts to prepare 5-nitro-2-acetylaminobenzyl benzoate from the corresponding alcohol have been unsuccessful. A rather interesting observation was made when attempts were being made to prepare 5-nitro-2-acetylaminobenzyl benzoate. 5-Nitro-2-acetylaminotoluene on being treated with bromine in chloroform solution (with iodine as catalyst) (Brewster, *J. Amer. Chem. Soc.*, 1918, **40**, 406) gave a bromo-compound which could not be crystallised. Assuming this to be 5-nitro-2-acetylaminobenzyl bromide, attempts were made to prepare the required ester by heating this in benzene solution with silver benzoate ; a product was thus isolated (m.p. 143-44°) but the analytical data showed that it was not the ester but corresponded more closely with 5-nitro-2-acetylaminobenzyl alcohol, m.p. 157-58°. But the mixed m.p. of the alcohol and this product was below 140° and they therefore cannot be identical. On

repeatedly extracting the supposed benzyl bromide from water only (without heating with silver benzoate), the same product was isolated. It was found to be soluble in alkali and gave a coloration with ferric chloride, showing the presence of a phenolic hydroxy group. Thus it appears that the product might probably be 5-nitro-2-acetylamino-3-hydroxytoluene formed according to the following scheme:



In this scheme it is found that bromine atom wanders from the nitrogen atom to position 3, but the replacement of the nuclear halogen by simple boiling with water is rather unusual.

In order to ascertain the effect, if any, of elongating the acyl group, which is used to protect the amino-group, the following compounds were also prepared: benzyl 5-nitro-2-propionylamino-benzoate, benzyl 5-nitro-2-*iso*butyrylaminobenzoate, the starting point in each case being 2-aminobenzoic acid ; these were converted into the propionyl and *iso*butyryl derivativas by heating with the respective acid chlorides. The acetylated products were then nitrated and the nitro-compounds were converted into the corresponding silver salts and heated with benzyl chloride as described before. The reduction of the nitro-compounds to the corresponding amines were carried out by aluminium-mercury couple as described in a previous communication (Niyogy, *J. Indian Chem. Soc.*, 1930, 7, 577); the only difference was that benzyl 5-nitro-2-acetylaminobenzoate was found to be very sparingly soluble in ether and so moist benzene was used as solvent. After the reducing operation, the bases were found to exhibit beautiful fluorescence. The stibinic acids were then prepared from these amines by the well-known diazo-reaction with careful regulation of temperature and quantity of alkali employed during the decomposition to prevent hydrolysis of the ester or the acyl group.

EXPERIMENTAL.

5-Nitro-2-acetylaminobenzoic Acid and 5-Nitro-2-acetylaminobenzyl Alcohol.—5-Nitro-2-acetylaminobenzaldehyde was prepared according to the method of Cohn and Springer (*loc. cit.*), the yield being 90 per cent. The nitroacetylaminobenzaldehyde (10 g) was gradually added to a solution of caustic potash (5 g.) in water (30 c.c.) cooled in ice to 0° and vigourously shaken after each addition. It was found that the whole of the aldehyde did not go into solution but the light yellow colour of the nitroaldehyde deepend as the reaction proceeded (time of addition 2 hours.). The reaction flask was then allowed to stand overnight in a refrigerator and the yellow viscous mass was then diluted with water. It was then repeatedly extracted with ether, till almost the whole of the solid had gone into solution. The ethereal layer was next dried over anhydrous sodium sulphate. On distilling off the ether, a yellow solid was obtained. Recrystallised from alcohol (twice) it had m. p. 197-98° (yield 80%). This product was found to be insoluble in alkali but fairly soluble in acids and to give diazo-reaction. It thus appears to be the free base and not the acetylated product. (Found: N, 17·02. $C_7H_8O_3N_2$ requires N, 16·66 per cent.).

The aqueous solution (after ether extraction) was acidified with hydrochloric acid when a light yellow solid separated. This was twice crystallised from dilute alcohol in long yellow needles, m. p. 267-68° (yield 75%). This product was found to be soluble in dilute sodium carbonate and to give diazo-reaction. It is therefore 5-nitro-2-aminobenzoic acid. (The m. p. of the acid as recorded by previous workers is 263-64°).

The *acetyl* derivative was prepared by heating the sample with acetic anhydride at 120-40° for 2 hours. It was crystallised from water as yellow needles, m. p. 216-17° (*cf.* Ullmann and Uzbachian, *loc. cit.*) (Found: N, 12·15. $C_9H_9O_5N_2$ requires N, 12·4 per cent.).

5-Nitro-2-acetylaminobenzyl Alcohol.—The required alcohol (4 g.) was heated at 140-50° for 2 hours with acetic anhydride (12 c.c.). On being poured into water an oily liquid separated which solidified after some time to a yellowish-brown mass. Recrystallised from alcohol it had m. p. 157-58°. (Found: N, 13·93. $C_9H_{10}O_4N_2$ requires N, 13·33 per cent.).

2-Acetylaminobenzoic Acid.—The methods which have been employed by the previous workers were not very convenient. Wheeler and Barnes (*Amer. Chem. J.*, 1898, **20**, 222) obtained

it by the action of acetyl chloride on the silver salt of aminobenzoic acid while Pawlewski (*Ber.*, 1898, **31**, 668) employed thioacetic acid and aminobenzoic acid. An easier and simpler method has now been found out.

o-Aminobenzoic acid (5 g.) was dissolved in acetic acid (20 c.c.). Acetic anhydride (10 c.c.) was then added when much heat was generated and a light brown crystalline solid immediately separated. On cooling, the solid was filtered off and washed with hot water till free from acid; m. p. 185-86° (yield 6 g.).

Nitration of 2-Acetylaminobenzoic Acid (*cf.* Rupe, *Ber.*, 1897, **30**, 1097).—Acetylanthranilic acid (20 g.) was gradually added to sulphuric acid (60 c.c.) with gentle agitation, till the whole of the solid had gone into solution. The acid solution was then cooled in ice water and a mixture of nitric acid (8 g., *d* 1·40) and sulphuric acid (20 c.c.) was slowly added with stirring (time 1 hour); the stirring was continued for another 30 minutes. The acid liquid was then poured into crushed ice. A light yellow viscous mass separated which solidified after some time. This was filtered off and washed free from acid and recrystallised from water, m. p. 157-58° (yield 22 g.). The substance was found to dissolve easily in dilute sodium carbonate solution but did not give diazo reaction. It appears to be identical with the product obtained by Rupe (*loc. cit.*). But on *re peating* this experiment, the nitrated product was found to have m. p. 216-17° (*cf.* Ullmann and Uzbachian, *loc. cit.*)

5-Nitro-2-acetylaminotoluene.—*o*-Acetotoluidide was gradually added to sulphuric acid (45 c.c.) cooled in ice, with mechanical stirring. After complete solution, a mixture of nitric acid (8 c.c., *d* 1·40) and concentrated sulphuric acid (15 c.c.) was slowly added. When the operation was concluded the acid solution was poured into crushed ice. A light pink coloured pasty mass separated which solidified after being allowed to stand for sometime. The solid was then filtered off, washed with water till free from acid and dried in *vacuo* over sulphuric acid. The product thus obtained (of a light pink colour) melted with decomposition at 101-4° (the m. p. of 5-nitro-2-acetylaminotoluene, described by Beilstein and Kuhlberg, *Z. Chem.*, 1871, *ii*, **7**, 99, is 102-3°) when however the raw product was crystallised twice from dilute alcohol, it melted at 197-98°. (Found: N, 14·52. $C_9H_{10}O_3N_2$ requires N, 14·43 per cent.).

As the m. p. of the nitrated products obtained by Beilstein and Kuhlberg (*loc. cit.*) was found to be different from that obtained during the course of this work, the identity of my product (m. p. 197-98°) was established in the following way.

The nitro-compound (2 g.) was added to water (200 c.c.) followed by magnesium sulphate (5 g.) The liquid was then heated up to boiling with vigorous stirring till the greater part of the nitro-compound had gone into solution. To this was then added powdered potassium permanganate (6 g.) in small quantities at a time and the stirring continued for 2 hours. Excess of permanganate was then destroyed by adding alcohol to the hot liquid and filtered off from the precipitated manganese dioxide. The filtrate, when acidulated with dilute sulphuric acid, deposited pale yellow needles which after recrystallisation melted at 216-17°. The m.p. was not depressed when mixed with another sample of 5-nitro-2-acetylaminobenzoic acid. It was found to be soluble in dilute alkali and did not give diazo-reaction. On warming with alkali, the acetyl group was removed and a product separated which melted at 263-64°. Thus it appears that the m.p. of 5-nitro-2-acetylaminotoluene is 197-98° and not 101° as given by Beilstein and Kuhlberg (*loc. cit.*).

Bromination of 5-Nitro-2-acetylaminotoluene.—5-Nitro-2-acetylaminotoluene (2·5 g.) was dissolved in chloroform and a crystal of iodine was added. The solution was heated under reflux on a water-bath and bromine (0·8 c.c.) in chloroform (10 c.c.) was slowly added to the boiling solution. At first no evolution of hydrobromic acid was noticed but after about 2 hours, fumes of hydrobromic acid were given off. After 4 hours, heating the reaction mixture was left overnight. Excess of solvent was then distilled off when a yellow pasty solid was left. Attempts to purify this were unsuccessful. This was taken up in benzene and heated under reflux with silver benzoate (2·5 g.) for 2 hours. A solid was found to have separated which was filtered off and the filtrate was evaporated to dryness. A brown oil was left which solidified in *vacuo*. The brown solid was repeatedly extracted with water and filtered. The united filtrates were then boiled with animal charcoal and again filtered. The filtrate on cooling gave a yellow needle shaped crystalline precipitate, m.p. 135-37°. Recrystallised from water (charcoal) it melted at 141-42°. (Found: C, 51·74; H; 4·99; N, 13·72. $C_9H_{10}O_4N_2$ requires C, 51·4 ; H, 4·76; N, 13·33 per cent.).

In another experiment, the residue left after evaporation of chloroform was repeatedly washed with water and the product that was isolated had m.p. 141-42° and analytical results identical with those obtained in the foregoing experiments.

Properties.—It dissolves in hot water and cold diute alkali. With ferric chloride a yellow coloration is produced. With diazotised aniline, an alkaline solution of the substance gave a red dye. It was found not to contain any halogen. Hence the conclusion is that the substance is a phenol, whose probable constitution is 5-nitro-2-acetylamino-3-hydroxytoluene.

2-*Propionylaminobenzoic Acid.*—This was prepared by heating 2-aminobenzoic acid (10 g.) and propionyl chloride (30 g.) in pyridine solution on a water-bath for 3 hours. The whole was then poured into water, when a brown oil separated which solidified on cooling and scratching. After several crystallisations from rectified spirit it melted at 120-21°. (Found: N, 8·04. $C_{10}H_{11}O_3N$ requires N, 7·23 per cent.).

5-*Nitro*-2-*propionylaminobenzoic Acid.*—The nitration of 2-propionylaminobenzoic acid was carried out by dissolving the substance in a mixture of sulphuric acid and acetic acid with good cooling. The raw nitration product first separated as an yellow oil which solidified after sometime and was purified by crystallising it (twice) from dilute alcohol in pale yellow needles, m.p. 199-200°. (Found: N, 11·8. $C_{10}H_{10}O_5N_2$ requires N, 12·24 per cent.).

2-iso*Butyrylaminobenzoic Acid.*—2-Aminobenzoic acid (12 g.) was added to benzene (about 100 c.c.) and treated with *iso*butyryl chloride (crude, 16 g.); the mixture was heated under reflux for six hours, till the acid had gone into solution and evolution of hydrochloric acid had almost ceased. Excess of benzene was then distilled off and the residue—a brown viscous mass—was left in vacuum overnight. The pasty solid thus obtained was dried on a porous plate, dissolved in benzene, boiled with animal charcoal and precipitated with the addition of benzine (twice) as white plates, m.p. 129-30°. (yield 10 g.). (Found: N, 7·3. $C_{11}H_{13}O_3N$ requires N, 6·78 per cent.).

Benzyl 5-Nitro-2-acetylaminobenzoate.—5-Nitro-2-acetylaminobenzoic acid (2 g.) was dissolved in acetone and treated with moist silver oxide. The precipitated silver salt was filtered off, washed with water and dried in *vacuo*. The dry mass was suspended in benzene, benzyl chloride (2 c.c.) was added and heated under

reflux for 6 hours. A yellowish-white solid was found to have separated, which was filtered off and found to be silver chloride. The benzene filtrate was evaporated when a yellow oil was left which solidified immediately. This was washed several times with alcohol, and then recrystallised from the same solvent in glistening white needles, m.p. 175-76°. (Found: N, 9·17. $C_{10}H_{10}O_5N_2$ requires N, 8·92 per cent.).

Benzyl 5-Nitro-2-propionylaminobenzoate.—This was prepared fromt he silver salt of 5-nitro-2-propionylaminobenzoic acid and benzyl chloride. The only difference being that the silver salt was prepared by adding silver nitrate to sodium 5-nitro-2-propionylaminobenzoate in water solution. The crude product was twice crystallised from alcohol, in pale yellow needles, m.p. 122-23°. (Found: N, 8·5. $C_{17}H_{16}O_5N_2$ requires N, 8·58 per cent.).

*Benzyl 5-Nitro-2-iso*butyrylaminobenzoate.—*iso*Butrylaminobenzoic acid (14 g.) was nitrated in sulphuric acid solution, with cooling in ice, with the required quantity of nitric acid (*d* 1 4). After the operation, the acid solution was poured into crushed ice, when a thick yellow oil separated. The water containing the greater part of acid, was decanted off and washed with fresh ice-cold water several times and allowed to stand overnight. The oil was thus converted into a yellow solid. But further purification of this was not attempted.

The raw nitration product was boiled with water and diluet sodium carbonate solution was added in small quantities at a time, till the brown oil which was formed on heating, had gone into solution. Excess of alkali was then destroyed by the addition of dilute nitric acid and filtered. The clear yellow filtrate was treated with silver nitrate when a yellowish solid separated. This was filtered off and dried in *vacuo* over sulphuric acid. The dry powder was suspended in benzene and converted into the benzyl ester as described before. The crude product obtained after evaporation of benzene, was dried on a porous plate and then crystallised from alcohol in long yellowish needles, m.p. 129-30°. (Found: N, 8·2. $C_{18}H_{18}O_5N_2$ requires N, 8·2 per cent.).

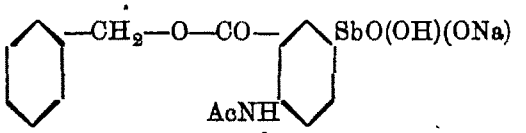
Benzyl 5-Amino-2-acetylaminobenzoate.—The reduction of the corresponding nitro-body was conducted in moist benzene solution with aluminium—mercury couple as described in a previous paper (*J. Indian Chem. Soc.*, 1930, 7, 575). The benzene solution, after being left overnight, was found to give green fluorescence. The

separated aluminium hydroxide was filtered off, the liquid dried over fused calcium chloride, filtered and treated with dry hydrochloric acid. The hydrochloride separated as a gelatinous mass. Dry ether was then added and left overnight. The faint pink precipitate was filtered off and dried in *vacuo*. It was dissolved in a mixture of chloroform and alcohol and precipitated with benzene, m.p. 219-20° (decomp). (Found: N, 9·04. $C_{16}H_{17}O_3N_2Cl$ requires N, 8·72 per cent.).

Benzyl 5-Amino-2-propionylaminobenzoate.—The reduction was carried out in ether solution with Al-Hg couple. The hydrochloride of the base was precipitated from the ether solution which dissolved in chloroform with a few drops of alcohol and precipitated with benzine; m.p. 187-88° (decomp). (Found: N, 8·24. $C_{17}H_{19}O_3N_2Cl$ requires N, 8·35 per cent.).

Benzyl 5-Amino-2-isobutyrylaminobenzoate.—The nitro-compound was reduced as described before. The hydrochloride was crystallised by dissolving it in chloroform (with a drop or two of alcohol) and petrol eum ether; m.p. 207-8° (decomp.). (Found: N, 7·95. $C_{18}H_{21}O_3N_2Cl$ requires N, 8·05 per cent.).

Benzyl Benzoate 2-Acetylamino-5-stibinate of Sodium



The required compound was prepared from benzyl 5-amino-2-acetylaminobenzoate, as described in previous communication. The sodium salt (light brown amorphous mass) was purified by dissolving in methyl alcohol and precipitating with ether as a faint pink mass. (Found: Sb, 26·4. $C_{16}H_{15}O_6NSbNa$ requires Sb, 26·08 per cent.).

Benzyl Benzoate 2-Propionylamino-5-stibinate of Sodium.—(Found: Sb, 24·8. $C_{17}H_{17}O_6NSbNa$ requires Sb, 25·3 per cent.).

Benzyl Benzoate 2-isoButyrylamino-5-stibinate of Sodium.—(Found: Sb, 26·1. $C_{18}H_{19}O_6NSbNa$ requires Sb, 25·5 per cent.).

My thanks are due to Prof. H. K. Sen for the interest he has taken in this work.

UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
DEPARTMENT OF APPLIED CHEMISTRY,
CALCUTTA.

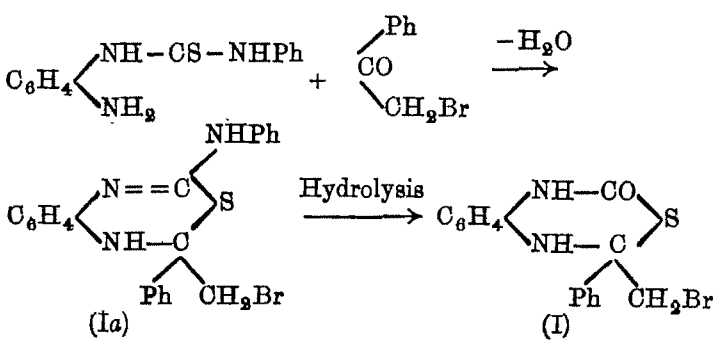
Received December 19, 1930.

Lengthened *ortho*-Di-derivatives of Benzene and their Ring-closure. Part VI.* Synthesis of Hepta-thiodiazines and Triazoles.

By Tejendra Nath Ghosh.

In a previous communication (Ghosh and Guha, *J. Indian Chem. Soc.*, 1929, **6**, 181) the reaction of 1-*o*-aminophenyl-3-arylthiocarbamides with thiocarbimides, carbimides, aldehydes, etc., was described and attention was directed to the behaviour of those compounds towards ring-closing agents In continuation of this work, it appeared to the author to be a matter of some interest to investigate the action of ω-bromoacetophenone, phosgene, etc., upon 1-*o*-aminophenyl-3-arylthiocarbamides.

1-*o*-Aminophenyl-3-phenylthiocarbamide reacts with ω-bromo-acetophenone to yield a compound possessing the composition, $C_{15}H_{13}ON_2SBr$ which can be represented by the formula (I). The reaction takes the following course.

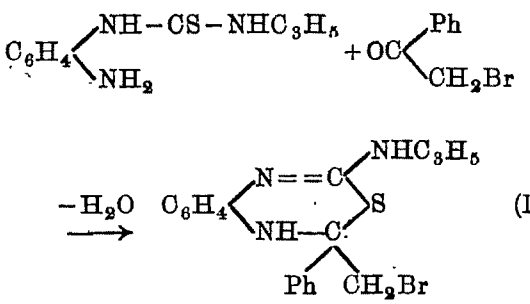


The constitutional formula (I) of the compound is supported by the fact that it is acidic in nature, being soluble in cold dilute alkali and precipitated by acids. It is not desulphurised by red oxide of mercury—which shows that the sulphur atom is present in the

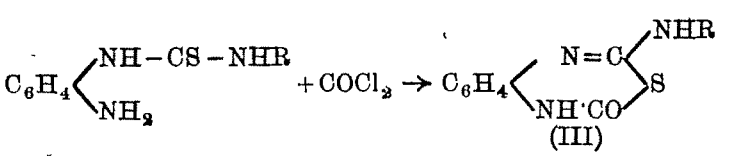
* The paper published in the *J. Indian Chem. Soc.*, 1929, **6**, 181 is Part V of this series.

molecule as a member of the ring (compare Busch, *Ber.*, 1901, **34**, 304; Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502). That the reaction actually takes the course as indicated above is further confirmed by the fact that a compound identical with compound (I) is obtained by condensing 1-*o*-aminophenyl-3-*p*-tolylthiocarbamide with ω-bromoacetophenone. The intermediate compound (Ia) could not be isolated and it is surprising how aniline could be eliminated so easily under the present experimental conditions. Bose (*J. Indian Chem. Soc.*, 1924, **1**, 53; 1925, **2**, 95) found that the condensation of thiosemicarbazides with ω-bromoacetophenone leads simultaneously to the formation of thiodiazine and thiodiazole derivatives accompanied by the elimination of water and hydrobromic acid. Guha (*J. Indian Chem. Soc.*, 1928, **5**, 153) also found an analogous reaction with 1-phenylthiocarbohydrazide, with this difference, however, that the reaction, in his case, proceeded only in one direction with the exclusion of the thiodiazole compound. It is, therefore, really interesting to note the different way in which the present reaction is taking place and this very fact brings forth an instance how the presence of groupings in the compounds exerts appreciable influence upon the course of the reactions.

1-*o*-Aminophenyl-3-allylthiocarbamide with ω-bromoacetophenone yields only the compound (II), thus:



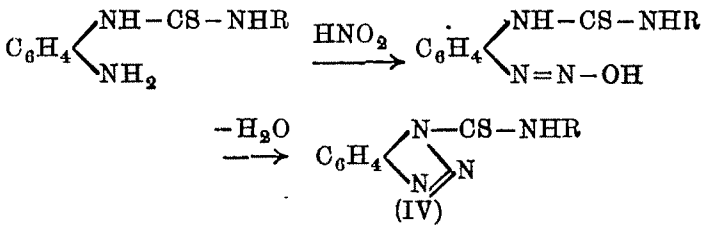
1-*o*-Aminophenyl-3-arylthiocarbamide reacts with phosgene to yield a heptathiodiazine derivative, thus:



where R = phenyl, *p*-tolyl, or 1:3:4-xylyl.

(*cf.* Busch, *J. pr. Chem.*, 1899, *ii*, **60**, 25; Guha and Roy-Choudhury, *J. Indian Chem. Soc.*, 1928, **5**, 164). The compound (III) is soluble in dilute alkali and does not possess any mercaptanic properties.

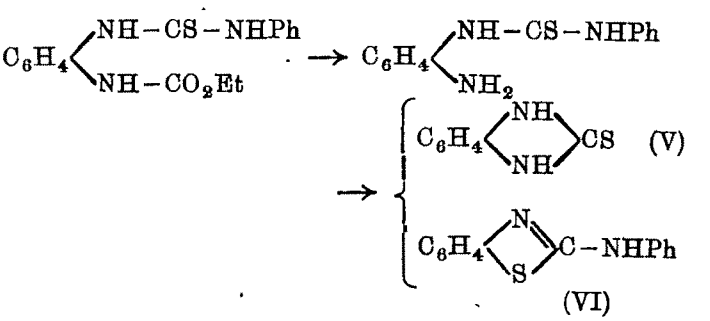
By the action of nitrous acid on 1-*o*-aminophenyl-3-arylthiocarbamide, a triazole derivative is obtained, thus:



where R = phenyl, *p*-tolyl or *m*-tolyl.

(compare Robinson and Thornley, *J. Chem. Soc.*, 1924, **125**, 2169). Freund and Schwarz (*Ber.*, 1896, **29**, 2491) obtained, by the action of nitrous acid on thiosemicarbazides, thiotriazole derivatives which evidently contain sulphur in the ring, whereas the present ring-closure is taking place through the nitrogen atom. The compound (IV) is acidic in nature being soluble in cold dilute alkali, is desulphurised by red oxide of mercury and liberate mustard oil on standing for a few hours.

o-Phenylthiocarbamidophenylurethane $EtO_2C-NH-C_6H_4-NH-CS-NHPh$ on treatment with 15 per cent. caustic potash solution yields a mixture of *o*-phenylenethiourea (V) and 2-phenylamino-4:5-benzo-1:3-thiazole (VI), thus:



The compound (V) was prepared by Ghosh and Guha (*loc. cit.*). Hofmann (*Ber.*, 1887, **20**, 1796) prepared the compound (VI) by the action of *o*-amidophenylmercaptan on phenylthiocarbimide.

Experimental.

2-Phenyl-2-bromomethyl-4:5-benzo-7-ketotetrahydro-1:3:6-heptathiodiazine (I).—An intimate mixture of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·5 g.) and ω-bromoacetophenone (2 g.) was boiled with dilute acetic acid (30 c.c.) for about half an hour. The clear dark brown solution, on standing yielded a white solid product which was twice crystallised from acetic acid in colourless needles, m. p. 230° (decomp.). (Found: N, 8·22; S, 8·22; Br, 23·25. $C_{15}H_{13}ON_2SBr$ requires N, 8·02; S, 9·17; Br, 22·92 per cent.) The presence of aniline in the acetic acid solution was confirmed by diazotisation and coupling with β-naphthol. The compound is soluble in cold dilute alkali and is precipitated by acids.

Action of ω-Bromoacetophenone upon 1-o-Aminophenyl-3-p-tolylthiocarbamide: Formation of (I).—The method of preparation was the same as in the case of the compound (I). The product was crystallised from acetic acid in colourless needles, m. p. 230° (decomp.). (Found: N, 8·30. $C_{15}H_{13}ON_2SBr$ requires N, 8·02 per cent.). The identity of this compound with the preceding compound was further confirmed by studying its properties which were similar to those of compound (I) and finally by taking the mixed melting point.

2-Phenyl-2-bromomethyl-4:5-benzo-7-allylaminodihydro-1:3:6-heptathiodiazine (II).—An intimate mixture of 1-*o*-aminophenyl-3-allylthiocarbamide (2·1 g.) and ω-bromoacetophenone (2 g.) was boiled with acetic acid under reflux for about half an hour. The clear dark brown solution, on standing yielded a white crystalline product which crystallised from acetic acid in colourless rectangular plates, m. p. 201-202°. It is insoluble in cold alkali and is not desulphurised by red oxide of mercury. (Found: N, 10·68; S, 8·63. $C_{18}H_{18}N_3SBr$ requires N, 10·82; S, 8·24 per cent.)

2-Keto-4:5-benzo-7-phenylaminodihydro-1:3:6-heptathiodiazine (III, R=Ph).—1-*o*-Aminophenyl-3-phenylthiocarbamide (2·5 g.) was dissolved in hot dry benzene to which the required quantity of phosgene (20 per cent. in toluene solution) was then added. A semi-solid mass came out and the solution was further boiled on the water-bath for an hour more. The semi-solid mass was purified by dissolving it in dilute caustic soda solution and precipitating by dilute hydrochloric acid. It crystallised from alcohol in colourless plates, m. p. 175-176°. It is not desulphurised by

red oxide of mercury. (Found: N, 15·83. $C_{14}H_{11}ON_3S$ requires N, 15·67 per cent.).

The *monomethyl* derivative crystallised from alcohol in shining colourless hexagonal prisms. m.p. 126-27°. (Found: N, 14·51. $C_{15}H_{13}ON_3S$ requires N, 14·83 per cent.).

2-*Keto*-4:5-*benzo*-7-p-*tolylaminodihydro*-1:3:6-*heptathiodiazine* (III, R=p-*tolyl*).—The method of preparation was the same as in the case of the previous compound. It crystallised from alcohol in colourless plates, m. p. 184-185°. (Found: N, 14·65. $C_{15}H_{13}ON_3S$ requires N, 14·84 per cent.)

2-*Keto*-4:5-*benzo*-7-(1:3:4)*xylylaminodihydro*-1:3:6-*heptathiodiazine* (III, R=1:3:4-*xylyl*).—It crystallised from alcohol in colourless plates, m. p. 173-174°. (Found: S, 10·49. $C_{16}H_{15}ON_3S$ requires S, 10·77 per cent.)

The *acetyl* derivative crystallised from acetic acid in fine colourless needles, m. p. 202-204°.

1-*Phenylthiocarbonamido*-4:5-*benzo*-1:2:3-*triazole* (IV).—An aqueous olution of sodium nitrite (1 g) was allowed to fall slowly from a separating funnel to an acetic acid solution of 1-*o*-aminophenyl-3-phenylthiocarbamide (2·5 g.) which was being cooled in a freezing mixture of ice and salt. The solution turned yellow and a yellowlish white crystalline substance came out which crystallised from ether in rectangular plates, m. p. 87-88°. It slowly liberates phenyl mustard oil on standing. (Found: N, 22·32; S, 12·31. $C_{13}H_{10}N_4S$ requires N, 22·04; S, 12·59 per cent.)

1-p-*Tolylthiocarbonamido*-4:5-*benzo*-1:2:3-*triazole* (IV, R=p-*tolyl*)—The method of preparation was identical. It was crystallised from ether in yellowish-white rectangular plates, m. p. 115°. (Found: S, 12·08. $C_{14}H_{12}N_4S$ requires S, 11·94 per cent.)

1-*o*-*Aminophenyl*-3-m-*tolylthiocarbamide*.—It was prepared according to the method of Lellmann (*Annalen*, 1885, **228**, 212) and was crystallised from benzene in shining colourless prisms, m. p. 144°. (Found: N, 16·12. $C_{14}H_{15}N_3S$ requires N, 16·34 per cent.)

1-m-*Tolylthiocarbonamido*-4:5-*benzo*-1:2:3-*triazole* (IV, R=m-*tolyl*).—The method of preparation was the same as in the case of the compound (IV). It crystallised from ether in yellowish-white rectangular plates, m. p. 94°. (Found: N, 21·26. $C_{14}H_{12}N_4S$ requires N, 20·89 per cent.)

Action of Potassium Hydroxide upon o-*Phenylthiocarbamidophenylurethane*: *Formation of* o-*Phenylenethiourea* (*V*) *and* 2-*Phenylamino*-

4:5-*benzo*-1:3-*thiazole* (VI).—*o*-Phenylthiocarbamidophenylurethane (5 g.) was heated on the water-bath with an excess of 15% potassium hydroxide solution for about 2 hours. The solution was then diluted with water, cooled and filtered from the white precipitate (VI) which, after being completely washed with hot water, was crystallised from alcohol in shining colourless plates, m. p. 158-159°. (Found: N, 12·84. $C_{13}H_{10}N_2S$ requires N, 12·38 per cent.). The alkaline solution, on acidification, yielded a product (V) which crystallised from hot water acidulated with a few drops of hydrochloric acid in shining colourless prisms, m. p. 301-302°. (Found: N, 18·45. $C_7H_6N_2S$ requires N, 18·66 per cent.). It is soluble in cold dilute alkali and gives a disulphide (m. p. 230°).

The author's best thanks are due Professor P. C. Guha, D.Sc., for the kind interest he has taken in this investigation.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore,

Received October 27, 1930.

Studies in Tetraphenylmethane Derivatives: Non-quinonoid Dyes. Part I.

By Rajendra Nath Sen and Sudhangsu Kumar Banerjee.

A careful perusal of the literature shows that the few tetraphenylmethane derivatives known at present were obtained mostly as by-products in some complicated reactions (Mackenzie, *J. Chem. Soc.*, 1901, **79**, 1209; Gomberg and Berger, *Ber.*, 1903, **36**, 1088; Copisarow, *J. Chem. Soc.*, 1917, **111**, 10; Ramm and Schmajewaki, *Helv. Chim. Acta*, 1921, **4**, 538), though a few attempts at the direct synthesis of simple derivatives are also recorded (Baeyer and Villiger, *Ber.*, 1902, **35**, 3013; Ullmann and Münzhuber, *Ber.*, 1903, **36**, 404; Boyd and Hardy, *J. Chem. Soc.*, 1928, p. 630, published when this work was in progress). In most of these cases, the derivatives were obtained in such poor yields as to be of little value in their systematic study. Further these derivatives are either monosubstituted (Baeyer and Villiger, *loc. cit.*, Ullmann and Münzhuber, *loc. cit.*) or di-substituted (Mackenzie, *loc. cit.*, Zincke and Wugk, *Annalen*, 1908, **363**, 284; Rassow, *J. pr. Chem.*, 1901, *ii*, **64**, 129) a few tri-substituted derivatives being also known (Zincke and Wugk, *loc. cit.*) with substitutions in not more than two nuclei.

The present work has been undertaken with a view to prepare tetraphenylmethane derivatives substituted in all the four nuclei and study their characteristics. The method, which has been found most convenient for this purpose, is to condense a triphenylcarbinol substituted in each of the three benzene nuclei with suitable mono-, di-, tri-, or tetra-substituted benzene derivatives, the condensation being effected by heating to 150—170° in the presence of freshly fused anhydrous sodium acetate. The reaction which takes place may be represented as follows:

$$(NH_2 \cdot C_6H_4)_3C \cdot OH + H \cdot C_6H_4 \cdot NH_2 = C(C_6H_4 \cdot NH_2)_4 + H_2O$$

As usual the hydrogen atom, in the *para*-position to the substituting group in the benzene derivatives, reacting with the OH-group of the carbinol, the condensation taking place in the *ortho*-position as well

when the *para*-position is occupied (as in the condensation of rosaniline base and *p*-hydroxybenzoic acid). This method is somewhat similar to that used by Baeyer and Villiger (*loc. cit.*) for the preparation of hydroxytetraphenylmethane and also by Ullmann and Münzhuber (*loc. cit.*) for the preparation of aminotetraphenylmethane and gives a very satisfactory yield (60 to 80 per cent.).

These tetraphenylmethane derivatives, substituted in all the four nuclei by NH_2- and OH-groups (with other groups in addition in some cases) are interesting not only because they have been prepared now for the first time but also on account of the remarkable observation that they are all more or less deeply coloured compounds and possess satisfactory dyeing properties, the amino-compounds, in general, producing on wool and silk, beautiful reddish to bluish-violet shades and the hydrdoxy-compounds yellow to pinkish shades.

It is evident from the structure of these compounds that they do not contain the so-called chromophores nor do they admit of any quinonoid configuration according to the accepted modes of tautomerisation and yet they are as good dyes as the triphenylcarbinol compounds, the colour and dyeing properties of which are generally attributed to their quinonoid transformation on salt formation. This appearance of colour and dyeing properties in compounds apparently devoid of the so-called chromophores may be accounted for by assuming that tetraphenylmethane itself is a colourless chromogen (like triphenylcarbinol) in which visible colour is developed (*i.e.*, the absorption band in the ultra-violet region is shifted into the visible part of the spectrum) by the introduction of suitable auxochromes into the various benzene nuclei. Similar tetraphenylmethane compounds with a pyrone ring possessing colour and marked dyeing properties have been previously described by Sen, Chattopadhyay and Sen-Gupta (*J. Indian. Chem. Soc.*, 1930, 7, 997) which also do not admit of any quinonoid configuration.

The following table gives a comparative study of the influence of different auxochromes on the colour and dyeing properties of the compounds described in the paper.

TABLE I.

No.	Compound (R = rosaniline base).	Colour and dyeing properties.	Remarks.
I.	$C(C_6H_4\cdot NH_2)_4$ (from R + aniline)	A delightful bluish-violet shade.	Contains one NH_2-group in each of the four benzene nuclei.
	$C(C_6H_4\cdot NH\,CH_3)_4$ by methylation of (I)	Bluer shade.	Alkylation of NH_2-groups, as in the triphenylmethane dyes, strengthens the auxochrome.*
II.	$(CH_3)_2NC_6H_4\cdot C(C_6H_4NH_2)_3$ (from R + dimethyl-aniline).	Slightly redder shade.	Effect of alkylation not very marked, the colour not being deepened.
III.	$AcNH\cdot C_6H_4\cdot C(C_6H_4NH_2)_3$ (from R + acetanilide).	Brownish-grey shade.	Acetylation of NH_2-groups weakens the auxochrome as usual.
	$C(C_6H_4\cdot NHAc)_4$ by acetylation of (I)	Slightly coloured; no dyeing property.	
	$C(C_6H_4\cdot NH\cdot CO\cdot C_6H_5)_4$ by benzoylation of (I)	Only a violet tinge.	Benzoylation of NH_2-groups also weakens the auxochrome.
IV.	$OH\cdot C_6H_4\cdot C(C_6H_4\cdot NH_2)_3$ (from R + phenol)	Light reddish-violet shade. (The affinity for the fibre is markedly impaired due to the presence of the acidic OH group in a basic dye.)	When a stronger auxochrome such as NH_2 is replaced by a weaker auxochrome, OH, there is generally a corresponding weakening of colour according as one or more NH_2-groups are replaced by OH.
V.	$CH_3O\cdot C_6H_4\cdot C(C_6H_4NH_2)_3$ (from R + anisole)	Shade much lighter than (I).	The affinity for the fibre is greater than that produced by (IV). Shade is lighter than (I) as one of the auxochromes is eliminated.

* Such slight anomalies are also noticed in the triphenylcarbinol dyes; for instance diaminotriphenylcarbinol gives a violet dye (Döbner's violet, while triaminotriphenylcarbinol gives a red dye rosaniline; tetramethyldiaminotriphenylcarbinol gives a green dye, malachite green while hexamethyltriaminotriphenylcarbinol gives a violet dye, crystal violet.

TABLE I—(*contd.*)

No.	Componnd (R = Rosaniline base).	Colour and dyeing properties.	Remarks.
VI.	$(OH)_2^{4}\,C_6H_3\cdot C(C_6H_4NH_2)_2$ (from R + resorcinol)	Reddish-violet shade.	Much better dye than (IV).
VII.	$(OH)_3^{3}\,C_6H_2\cdot C(C_6H_4NH_2)_2$ (from R + pyrogallol)	,,	,,
VIII-X.	$(OH)(COOH)\cdot C_6H_3\cdot C(C_6H_4NH_2)_2$ (from R + salicylic acid, *p*-hydroxybenzoic acid, or *m*-hydroxybenzoic acid).	Much deeper shade (bluer)	The carboxy group exerts a remarkable influence in augmenting the depth of colour, stronger effect being produced with the CO_2H group in *ortho*-position.
XI.	$(OH)(CO_2H)C_6H_2(Me)\cdot C(C_6H_4\cdot NH_2)_2$ (from R + *o*-cresotinic acid)	Beautiful violet shade; (much bluer than (VIII).	Effect of the CH_3 group.
XII.	$(OH)_3(CO_2H)\cdot C_6H\cdot C(C_6H_4NH_2)_2$ (from R + gallic acid)	Slightly redder than (VII).	Effect of the CO_2H group on trihydroxytriaminotetraphenylmethane is not very marked.
	Tri-, tetra-, penta-, hexa-hydroxy-derivatives (obtained from II, III, IV, I, VI and VIII by diazo eaction).	Very light shades of yellow to pink.	A minimum of three hydroxyl groups in three different nuclei being required for the development of yellow colour.

From the above table it is evident that the amino-compounds are better dyes than the hydroxy-compounds, a minimum of three auxochromes being required in either case for the development of fairly deep colour and dying property.

Two very interesting observations have also been made in the case of the amino-compounds in general (having at least three NH_2 groups). (*a*) The colour in strong mineral acid solution undergoes a remarkable change on dilution.* (*b*) Different dye shades on wool and silk are produced according as the dyeing takes place from an acetic acid or a mineral acid bath ; the shades in the latter case being bluer. The hydroxy-compounds have also an interesting property, their solutions in caustic alkalis and ammonia exhibiting slight fluorescence.

Experimental.

Symmetrical p-*Tetra-aminotetraphenylmethane*, $C(C_6H_4.NH_2)_4$. —*p*-Rosaniline base (2·5 g.), freshly distilled aniline (5 g.) and fused sodium acetate (10 g.) are heated together at 160° for 8 hours. The excess of aniline is distilled off in steam and the product extracted with 5*N*-hydrochloric acid. The acid solution is filtered and made alkaline with ammonia. The precipitate is filtered off and washed with boiling water and dried. The powdered mass is then washed with boiling chloroform and ether and then crystallised from alcohol in shining violet-black leaflets (not melting up to 280°), soluble in alcohol, acetone, mineral acids (bluish-violet solution), and acetic acid (reddish-violet solution) and insoluble in chloroform, benzene, and ether. The acetic acid solution dyes wool and silk bluish-violet, while mineral acid solutions dye a much bluer shade. Yield 70%. (Found: N, 14·06. $C_{25}H_{24}N_4$ requires N, 14·74 per cent.)

The *tetramethyl* derivative was prepared by methylating the above compound. It crystallised from alcohol as fine shining microcrystalline powder, soluble in acetone, alcohol (reddish-violet solution), acetic acid (bluish-violet solution), mineral acids (greenish-blue solution), and insoluble in ether, benzene and chloroform. It dyes wool and silk a light blue shade from acetic acid bath. The affinity for fibre is rather weak. Yield 70%. (Found:

* A strong acid solution of $C(C_6H_4.NH_2)_4$ is greenish-yellow which on dilution changes to bluish-violet; the strong acid solution of $Me_2N.C_6H_4.C(C_6H_4NH_2)_3$ is blue which on dilution changes to deep bluish-violet.

C, 79·5 ; H, 7·6; N, 12·6. $C_{29}H_{32}N_4$ requires C, 79·81; H, 7·34; N. 12·84 per cent.)

The *monoacetyl* derivative was prepared by condensing *p*-rosaniline-base and acetanilide at 150° for 8 hours, subsequent operations being same as in (I) (yield 60%). It formed greyish-violet microcrystalline powder (not melting up to 250°), sparingly soluble in absolute alcohol, fairly soluble in acetic acid ; insoluble in benzene, ether and chloroform. The acetic acid solution dyes wool and silk brownish-grey. (Found: N, 12·96. $C_{27}H_{26}ON_4$ requires N, 13·22 per cent.)

The *sym.-tetra-acetyl* derivative was prepared from (I) by acetylation, and formed dark grey powder, m.p. 218° (decomp.) soluble in glacial acetic acid, having no tinctorial property. (Found: N. 10·71. $C_{33}H_{32}O_4N_4$ requires N, 10·2 per cent.)

The *sym.-tetrabenzoyl* derivative was prepared by benzoylating (I). It is almost colourless and has no tinctorial property. (Found: N, 6·5. $C_{53}H_{40}O_4N_4$ requires N, 7·04 per cent.)

A *dimethyl* derivative (II) was prepared by condensing *p*-rosaniline base with dimethylaniline as in (I). It formed greyish-violet micro-crystalline powder (not melting up to 280°, soluble in alcohol, acetic acid and acetone ; insoluble in benzene, chloroform, and ether. The acetic acid bath dyes wool and silk a beautiful reddish-violet shade (yield 70%). (Found: N, 14·05. $C_{27}H_{28}N_4$ requires N, 13·72 per cent.)

Tri-p-*hydroxy*-p *dimethylaminotetraphenylmethane*.—It was prepared by diazotizing a hot acetic acid solution of the above dimethyl compound with sodium nitrite in the usual manner. The precipitated hydroxy-compound is filtered, dissolved in a freshly prepared solution of caustic soda and reprecipitated with an excess of 5*N*-sulphuric acid, again filtered, dried and crystallised from alcohol as dark-brown microcrystalline powder (not melting up to 250°) soluble in caustic alkalis and ammonia giving slightly fluorescent solution and sparingly soluble in absolute alcohol. The ammonium salt solution dyes wool and silk light turmeric yellow shades (yield 80%). (Found: N, 3·1. $C_{27}H_{25}O_3N$ requires N, 3·4 per cent.)

p-*Hydroxytri*-p-*aminotetraphenylmethane* (IV) was prepared by condensing phenol (carefully dried in a desiccator) and *p*-rosaniline base for 6 hours at 150°. The subsequent operations are same as in (I) (yield 60%). It is a greyish-violet microcrystalline powder, melts at 170° (decom.) sparingly soluble in dilute mineral acids, freely in glacial acetic acid, also soluble in alcohol, acetone and

dilute caustic alkalis (to some extent on warming) ; insoluble in chloroform, ether and benzene. Its affinity for fibre is very weak; the acetic acid solution dyes wool and silk a light reddish-violet shade. (Found: N, 10·3. $C_{25}H_{23}ON_3$ requires N, 11·02 per cent.)

p-*Methoxytri*-p-*aminotetraphenylmethane* (V) was prepared by condensing *p*-rosaniline base and anisole as in the above case (yield 60%). It is a greyish-violet microcrystalline powder (not melting up to 260°), soluble in alcohol. acetone, mineral acids and acetic acid (reddish-violet solution) ; insoluble in ether, benzene and chloroform. The acetic acid bath dyes wool and silk a dull reddish-violet shade. (Found: N, 10·34. $C_{26}H_{25}ON_3$ requires N, 10·63 per cent.)

p-*Methoxytri*-p-*hydroxytetraphenylmethane* was prepared from (V) by the diazo reaction (yield 80%). It is a shining grey powder (not melting up to 250°) soluble in caustic alkalis, ammonia and absolute alcohol, insoluble in acids, benzene, ether and chloroform. The ammonium salt solution dyes wool and silk a light yellow shade. (Found: C, 78·0 ; H, 5·9. $C_{26}H_{22}O_4$ requires C, 78·4; H, 5·53 per cent.)

p-*Tetrahydroxytetraphenylmethane* was prepared from (I) by the diazo reaction (yield 80 per cent.). It formed shining dark brown leaflets (not melting up to 260°), soluble in alkalis and ammonia with slight flourescence and also in alcohol, insoluble in acids, ether, and benzene. The ammonium salt solution dyes wool and silk a decent light-yellow shade. (Found: C, 77·9; H, 6·9. $C_{25}H_{20}O_4$ requires C, 78·12; H, 6·67 per cent.)

Tetra-silver salt was prepared by adding silver nitrate to the cold ammonium salt solution. The precipitated is allowed to settle in the dark, then quickly filtered and dried in a vacuum desiccator kept also in a dark chamber. (Found: Ag 52·7. $C_{25}H_{16}O_4Ag_2$ requires Ag, 53·2 per cent.)

Tri-p *hydroxy*-p-*acetylaminotetraphenylmethane* was prepared from the mono-acetyl derivative of (I) by the diazo reaction (yield 70 per cent.). The ammonium salt solution dyes wool and silk a light pinkish-yellow shade. (Found: N, 3·1. $C_{27}H_{23}O_4N$ requires N, 3·3 per cent.)

Tri-p-*amino*-2:4-*dihydroxytetraphenylmethane* (VI).—It was prepared by condensing resorcinol and *p*-rosaniline base at 155° for 8 hours. The excess of resorcinol is removed by boiling water. It is crystallised from alcohol as violet micro-crystalline powder, m.p.

160° (decomp.), soluble in alcohol, acetic acid and dilute mineral acids; slightly soluble in acetone, insoluble in water, ether, benzene and chloroform. The acetic acid solution dyes wool and silk a reddish-violet shade; while mineral acid bath gives a light bluish-violet shade (yield 60 per cent.). (Found: N, 9·96. $C_{25}H_{23}O_2N_3$ requires N, 10·58 per cent.)

Tri-p-*hydroxy*-2:4-*dihydroxytetraphenylmethane* was prepared from (VI) (yield 80 per cent.). It formed reddish-brown leaflets, (not melting up to 250°) soluble in caustic soda (deep orange-red solution with slight fluorescence), in ammonia (slightly fluorescent) and in absolute alcohol; insoluble in acids, ether, benzene and chloroform. The ammonium salt solution dyes wool and silk a pinkish shade. (Found: C, 74·3; H, 4·5. $C_{25}H_{20}O_5$ requires C, 75·00; H, 4·00 per cent.)

Penta-silver Salt.—(Found: Ag, 57·6. $C_{25}H_{15}O_5Ag_5$ requires Ag, 57·75 per cent.).

Tri-p-*amino*(2:3:4)-*trihydroxytetraphenylmethane* (VII) was prepared by condensing pyrogallol and *p*-rosaniline base at 166° (yield 80 per cent.). It is a dark violet micro-crystalline powder, (not melting up to 260°), fairly soluble in hot dilute mineral acids and glacial acetic acid; sparingly soluble in alcohol. Dyes wool and silk a bluish-violet shade from an acetic acid bath. The dyeing affinity is weak. (Found: N, 10·5. $C_{25}H_{23}O_3N_3$ requires N, 10·17 per cent.)

Tri-p-*hydroxy*-2:3:4-*trihydroxytetraphenylmethane* was prepared from (VII) (yield 70 per cent.). (Found: C, 71·8; H, 5·00. $C_{25}H_{20}O_6$ requires C, 72·1; H, 4 80 per cent.)

Hexa-silver Salt.—(Found: Ag, 60·12. $C_{25}H_{14}O_6Ag_6$ requires Ag, 61·2 per cent.).

Tri-p-*amino*-p-*hydroxytetraphenylmethane*-m-*carboxylic acid* (VIII) was obtained by condensing *p*-rosaniline base and salicylic acid at 150°, subsequent operations being same as in (VI) (yield 70 per cent.). It formed violet micro-crystalline powder (not melting up to 260°). Acetic Acid bath dyes reddish-violet while mineral acid bath dyes bluish-violet shades. It gives a slight effervescence with a dilute alcoholic solution of sodium bicarbonate. (Found: N, 9·75. $C_{26}H_{23}O_3N_3$ requires N, 9·9 per cent.)

Tetra-p-*hydroxytetraphenylmethane*-m-*carboxylic Acid.*—It was prepared from (VIII) as usual (yield 60 per cent.). It is a brownish micro-crystalline powder (not melting up to 260°).

soluble in caustic alkalis and ammonia (slight fluorescence) and absolute alcohol; insoluble in ether, benzene and chloroform; it effervesces slightly with a dilute alcoholic solution of sodium bicarbonate. The ammonium salt solution dyes wool and silk a light yellow shade. (Found: C, 72·7; H, 4·8. $C_{26}H_{20}O_6$ requires C, 72·9; H, 4·6 per cent.)

Tri-p-*amino*-p-*hydroxytetraphenylmethane*-o-*carboxylic acid* (IX) was prepared by condensing *p*-rosaniline base and *m*-hydroxybenzoic acid at 170° (yield 70 per cent.). It is a dark violet microcrystalline powder (not melting up to 250°), sparingly soluble in mineral acids, freely in acetic acid and in absolute alcohol; insoluble in chloroform, benzene and ether. Dilute alcoholic solution effervesces slightly with a dilute solution of sodium bicarbonate.

The acetic acid solution dyes wool and silk a deep bluish-violet shade. (Found: N, 9·48. $C_{26}H_{23}O_3N_3$ requires N, 9·9 per cent.)

Tetra-p-*hydroxytetraphenylmethane*-o-*carboxylic acid* was prepared from (IX) (yield 70 per cent.) Dark brown micro-crystalline powder (not melting up to 200°). Soluble in alkalis, ammonia and alcohol; insoluble in acid, benzene, ether and chloroform. The ammonium salt solution dyes wool and silk a light pink shade. (Found: C, 72·6; H, 4·9. $C_{26}H_{20}O_6$ requires C, 72·9; H, 4·6 per cent.).

Tri-p-*amino*-o-*hydroxytetraphenylmethene*-m-*carboxylic Acid* (X).—It is prepared by condensing *p*-rosaniline base and *p*-hydroxybenzoic acid at 170° for 8 hours, subsequent operations being same as in (VIII). It is a violet microcrystalline powder (not melting up to 250°), soluble in mineral acids (dull violet solution), acetic acid (bluish-violet solution) and alcohol; produces bluish-violet shade on wool and silk from acetic acid bath; the shade obtained from mineral acid baths is much bluer. (Found: N, 9·89. $C_{26}H_{23}O_3N_3$ requires N, 9·9 per cent.).

Tri-p-*hydroxy*-o-*hydroxytetraphenylmethane*-m-*carboxylic acid* was prepared from the above. Dark brown micro-crystalline powder, soluble in caustic alkalis, ammonia and alcohol; insoluble in chloroform, ether, benzene and acid. The ammonium salt solution dyes wool and silk a bright yellow shade. (Found: C, 72·6; H, 4·9. $C_{25}H_{20}O_6$ requires C, 72·9; H, 4·6 per cent.).

Tri-p-*amino*-p- *hydroxy*-m-*methyltetraphenylmethane*-m-*carboxylic Acid* (XI).—It was prepared by condensing *p*-rosaniline base and *o*-cresotinic acid at 165° exactly as in (VIII) (yield 80 per cent.) It

formed shining violet crystalline powder (melting at 87°-90°), soluble in mineral acids (greenish-blue solution), acetic acid (bluish-violet solution) and absolute alcohol (violet solution); insoluble in ether, benzene and chloroform.

It effervesces slightly with a dilute alcoholic solution of sodium bicarbonate; acetic acid bath dyes wool and silk a brilliant bluish-violet shade, the shade obtained from a mineral acid bath being much bluer. (Found: N, 10·1. $C_{27}H_{25}O_3N_3$ requires N, 9·6 per cent.).

Tetra-p-*hydroxy*-m-*methyltetraphenylmethane*-m-*carboxylic acid*, $(CO_2H)(OH)(Me)\cdot C_6H_2\cdot C(C_6H_4\cdot OH)_3$ was prepared from the above (yield 60 per cent.). It formed dark brown micro-crystalline powder (not melting up to 250°), soluble in alkalis, ammonia and alcohol; insoluble in chloroform, ether and benzene. The ammonium salt solution dyes wool and silk a light yellow shade. (Found: C, 73·00; H, 5·2. $C_{27}H_{22}O_6$ requires C, 73·3; H, 4·98 per cent.).

Tri-p-*amino*-2:3:4-*trihydroxytetraphenylmethane*-o-*carboxylic Acid* (XII).—It was prepared by condensing *p*-rosaniline base and gallic acid at 179° for 8 hours, subsequent operations being same as in (VIII) (yield 70 per cent.). It fromed reddish-violet micro-crystalline powder (not melting up to 250°), soluble in mineral acids, acetic acid, alcohol and acetone; insoluble in ether, benzene and chloroform; acetic acid bath dyes wool and silk a reddish-violet shade. (Found: N, 8·3. $C_{26}H_{23}N_3O_8$ requires N, 9·1 per cent.).

Tri-p-*hydroxy*- 2:3:4-*trihydroxytetraphenylmethane* -o- *carboxylic acid* was prepared from the above by the diazo reaction (yield 60 per cent.). It fromed dark brown micro-crystalline powder (not melting up to 250°), soluble in alkalies, ammonia and alcohol; insoluble in acids, ether, benzene and chloroform. The ammonium salt solution dyes wool and silk a straw yellow shade. (Found: C, 67·5; H, 4·7. $C_{26}H_{20}O_8$ requires C, 67·83; H, 4·35 per cent.).

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.

Received November 7, 1930.

Interaction between Polybasic Acids and Neutral Salts. Part I. *ortho*-Phosphoric Acid.

By Subodh Kumar Majumdar.

The dissociation constants of *ortho*-phosphoric acid, determined by different methods differ considerably (Abbot and Bray, *J. Amer. Chem. Soc.*, 1909, **31**, 729 ; Michaelis and Garmedia, *Biochem. Z.*, 1914, **67**, 413 ; Michaelis and Krüger, *Biochem. Z.*, 1921, **119**, 307 ; Prideaux and Ward, *J. Chem. Soc.*, 1924, **125**, 423 ; Noyes and Sherrill, *J. Amer. Chem. Soc.*, 1926, **48**, 1861 ; Kolthoff, *Rec. trav. chim.*, 1927, **46**, 350).

In the present paper the activities of the hydrogen ion determined from measurements of electromotive force in mixtures of phosphoric acid with chloride, bromide and iodide of potassium are recorded. In some instances measurements with Thymol Blue have been made using a Helige Immersion Colorimeter.

The thermodynamic dissociation constant K of a monobasic acid, defined by the equation

$$K = \frac{a_+ a_-}{a_1}, \qquad \ldots \quad (1)$$

should be independent of the concentration of the acid, provided the same solvent is used; a_+, a_- and a_1 are respectively the activities of the hydrogen ion, anion and the neutral molecule.

In *dilute* solutions of neutral salt, it is generally assumed that the thermodynamic dissociation constant is constant and independent of the nature of the salt. It is also sometimes assumed that the activity coefficient of the undissociated molecule is independent of the ionic strength and is taken to be unity (Larsson, *Z. anorg. Chem.*, 1926, **155**, 247 ; Noyes and Sherrill, *loc. cit.*; McInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068; Cohn, *ibid.*, 1927, **49**, 178). We have thus

$$K = \frac{\gamma_H C_H \gamma_A C_A}{C_{HA}} \qquad \ldots \quad (2)$$

The first dissociation constant of phosphoric acid is moderately strong. At concentrations above ·001*M* it can be treated as a monobasic acid and C_H and $C_{H_2PO_4}$ can be taken to be identical without sensible error. Hence we get

$$K_1 = \frac{a^2_H}{C_{H_3PO_4}} \qquad \ldots \qquad (3)$$

It would appear from the following data that at near about normal concentrations of the halides, there is a sudden increase in the activity.

Experimental.

A Leeds and Northrup K-type potentiometer was used. A Dolezalek-type hydrogen electrode vessel, made of borosilicate glass with ground stopper, was employed (Mukherjee and Kumar, *J. Amer. Chem. Soc.*, 1930, **52**, 2179). Merck's pure phosphoric acid (d, 1·7) was made into a stock solution and the strength determined gravimetrically. A few drops of toluol were added to it. The salts employed were of Merck's Reagent quality. The concentrations are given in gm. molecules per 1000 gm. of water. A saturated KCl bridge was used. A second vessel containing the solution was interposed between the hydrogen electrode and the salt bridge and connected with the latter by an inverted U-shaped syphon tube. The lower portion of the syphon tube was used to effect connection between the salt bridge and solution and the vertical limb was closed. The thermostat was maintained at 35°. The electromotive force of the calomel vessel was measured against 0·1*N*-HCl with identical arrangement and this was found to be 0·3482 volt. The activity coefficient of ·1*N*-HCl at 35° was taken to be ·7956 (Mukherjee and Kumar, *loc. cit.*). Reduction of phosphoric acid by hydrogen in presence of platinum does not appear to take place as the electromotive force remains constant over fairly long periods (3 hours) and is generally reproducible.

TABLE I.

$H_3PO_4 = 0{\cdot}033\ M.$

Conc. of salt (M).	E.M.F. (Corrected)	p_H Electrometric.	p_H Colorimetric.
0	0·3975	1·90	1·96
·01 KCl	0·3975	1·90	1·99
·1	0·3975	1·90	1·98
1·032	0·3920	1·81	—
·01 KBr	0·3972	1·90	1·96
·1	0·3963	1·88	1·97
1·040	0·3888	1·76	1·78
·01 KI	0·3972	1·90	1·96
·1	0·3963	1·88	1.97
1·051*	0·3981	1·77	—

TABLE II.

$H_3PO_4 = 0{\cdot}0033\ M.$

Conc. of salt (M).	E. M. F. (Corrected)	p_H Electrometric.	p_H Colorimetric.
0	·4424	2·64	2·7
·01 KCl	·4422	2·64	2·7
·1	·4424	2·64	2·7
1·033	·4386	2·58	2 59
·01 KBr	·4408	2·61	2·63
·1	·4408	2·61	2·61
1·040	·4360	2·53	2·59
·01 KI	·4412	2.62	2·65
·1	·4418	2·63	2·66
1·051*	·4400	2·60	—

* At this concentration free iodine is liberated; on continued passage of hydrogen, HI is formed and the colour is discharged.

TABLE III.

$H_3PO_4 = 0{\cdot}033\ M.$

Conc. of salt (M).	a_H (exp.) $\times 10^2$	γ	$C_H = \frac{a_H}{\gamma}$.	$C_{H_3PO_4} = C - C_H$.	$K_1 = \frac{a^2_H \text{ (exp.)}}{C_{H_3PO_4}}$.	$K'_1 = \frac{a^2_H \text{ (exp.)}}{C}$.
0	1·26	·850	$1{\cdot}48 \times 10^{-2}$	$1{\cdot}85 \times 10^{-2}$	$8{\cdot}58 \times 10^{-3}$	$4{\cdot}77 \times 10^{-3}$
·01 KCl	1·26	·834	$1{\cdot}51 \times 10^{-2}$	$1{\cdot}82 \times 10^{-2}$	$8{\cdot}72 \times 10^{-3}$	$4{\cdot}77 \times 10^{-3}$
·1	1·26	·782	$1{\cdot}61 \times 10^{-2}$	$1{\cdot}72 \times 10^{-2}$	$9{\cdot}23 \times 10^{-3}$	$4{\cdot}77 \times 10^{-3}$
1·08	1·55	·708	$2{\cdot}19 \times 10^{-2}$	$1{\cdot}14 \times 10^{-2}$	$2{\cdot}10 \times 10^{-3}$	$7{\cdot}21 \times 10^{-3}$
·01 KBr	1·26	·834	$1{\cdot}51 \times 10^{-2}$	$1{\cdot}82 \times 10^{-2}$	$8{\cdot}72 \times 10^{-3}$	$4{\cdot}77 \times 10^{-3}$
·1	1·32	·782	$1{\cdot}69 \times 10^{-2}$	$1{\cdot}64 \times 10^{-2}$	$1{\cdot}06 \times 10^{-2}$	$5{\cdot}28 \times 10^{-3}$
1·04	1·74	·707	$2{\cdot}46 \times 10^{-2}$	$8{\cdot}7 \times 10^{-3}$	$3{\cdot}48 \times 10^{-2}$	$9{\cdot}09 \times 10^{-3}$
·01 KI	1·26	·834	$1{\cdot}51 \times 10^{-2}$	$1{\cdot}82 \times 10^{-2}$	$8{\cdot}72 \times 10^{-3}$	$4{\cdot}77 \times 10^{-3}$
·1	1·32	·782	$1{\cdot}69 \times 10^{-2}$	$1{\cdot}64 \times 10^{-2}$	$1{\cdot}06 \times 10^{-2}$	$5{\cdot}28 \times 10^{-3}$
1·05	1·70	·707	$2{\cdot}40 \times 10^{-2}$	$9{\cdot}3 \times 10^{-3}$	$3{\cdot}10 \times 10^{-2}$	$8{\cdot}68 \times 10^{-3}$

TABLE IV.

$H_3PO_4 = 0{\cdot}0033\ M.$

Conc. of salt (M.)	a_H (exp.) $\times 10^3$	γ	$C_H = \frac{a_H}{\gamma}$.	$C_{H_3PO_4} = C - C_H$.	$K_1 = \frac{a^2_H \text{ (exp.)}}{C_{H_3PO_4}}$.	$K'_1 = \frac{a^2_H \text{ (exp.)}}{C}$.
0	2·29	·941	$2{\cdot}43 \times 10^{-3}$	$9{\cdot}0 \times 10^{-4}$	$5{\cdot}82 \times 10^{-3}$	$1{\cdot}57 \times 10^{-3}$
·01 KCl	2·29	·892	$2{\cdot}56 \times 10^{-3}$	$7{\cdot}7 \times 10^{-4}$	$6{\cdot}81 \times 10^{-3}$	$1{\cdot}57 \times 10^{-3}$
·1	2·29	·779	$2{\cdot}94 \times 10^{-3}$	$3{\cdot}9 \times 10^{-4}$	$1{\cdot}34 \times 10^{-2}$	$1{\cdot}57 \times 10^{-3}$
1·08	2·63	·705	$3{\cdot}78 \times 10^{-3}$	—	—	$2{\cdot}08 \times 10^{-3}$
·01 KBr	2·45	·892	$2{\cdot}74 \times 10^{-3}$	$5{\cdot}9 \times 10^{-4}$	$1{\cdot}01 \times 10^{-2}$	$1{\cdot}80 \times 10^{-3}$
·1	2·45	·779	$3{\cdot}14 \times 10^{-3}$	$1{\cdot}9 \times 10^{-4}$	$3{\cdot}16 \times 10^{-2}$	$1{\cdot}80 \times 10^{-3}$
·104	2·95	·703	$4{\cdot}19 \times 10^{-3}$	—	—	$2{\cdot}61 \times 10^{-3}$
·01 KI	2·40	·892	$2{\cdot}69 \times 10^{-3}$	$6{\cdot}4 \times 10^{-4}$	$9{\cdot}00 \times 10^{-3}$	$1{\cdot}73 \times 10^{-3}$
·1	2·34	·779	$3{\cdot}00 \times 10^{-3}$	$3{\cdot}3 \times 10^{-4}$	$1{\cdot}66 \times 10^{-2}$	$1{\cdot}64 \times 10^{-3}$
1·05	2·51	·703	$3{\cdot}57 \times 10^{-3}$	—	—	$1{\cdot}89 \times 10^{-3}$

The concentration of the undissociated phosphoric acid has been calculated as follows: Kolthoff (*loc. cit.*) obtained value of K_1 ranging between 8·5 and $9{\cdot}5\times10^{-3}$ between the concentrations ·001 *M* and ·1*M*. a_H can be calculated from the following equation usuing the mean value:—

$$a_H = -\frac{K_1}{2} + \tfrac{1}{2}\sqrt{K_1^2 + 4\,K_1 C} \qquad \ldots \quad (4)$$

where *C*, is the concentration of the acid. Assuming as a first approximation that the activity coefficient is unity, a_H as determined above can be put as C_H and this value can be subsequently used in calculating the ionic strength of the ions formed from of the acid. The activity coefficient is then obtained from Harned's formula (*J. Amer. Chem. Soc.*, 1926, **48**, 326), assuming that the mean activity coefficient of ions formed by the first dissociation of phosphoric acid is the same as that for HCl of corresponding mixtures.

The concentration of hydrogen ion is obtained by dividing the activity of hydrogen ion by the activity coefficient so found. Evidently it is being assumed that HCl is completely dissociated at these concentrations, for in calculating activity coefficient, the total concentration is used. The concentration of undissociated phosphoric acid is obtained by difference, assuming that the other stages of dissociation occur in negligible amounts.

Discussion.

The error in the value of K_1 arising out of the uncertainties of the liquid—junction potential does not appear to be great. The values obtained for the more concentrated acid solutions at lower concentrations of salt are in substantial agreement with those obtained by Kolthoff (*loc. cit.*). The low value for the more dilute acid solutions observed in the absence of the neutral salt may be ascribed in part to the errors of measurement of hydrogen-ion activity at such concentrations. The relative variation in the activity is much less subject to the errors arising out of uncertainties of the liquid—junction potential. It is rather striking that the activity remains constant up to ·1*N* salt solution, although the ionic strength changes about 3 times. The increase of K'_1 with ionic strength is to be referred to the constancy of the activity and the method of calculation,

On the other hand, using total concentrations as in K'_1, the constant is found to be fairly independent of the salt concentration up to ·1*N*. The inconstancy of K_1 can scarcely be accounted for from considerations of changes of the activity coefficients of the undissociated molecules, for it would require variation of the activity coefficient of the neutral molecule by several hundred per cent. It cannot also be accounted for by considerations of changes in the junction potential. It is difficult to believe that variation in the junction potential will exactly balance the changes in the activity. The constancy in the observed activity requires an explanation. Moreover the activities for the two dilutions of the acid are in a constant ratio up to ·1 *N* salt concentration. The ratio of the activities for the two concentrations of the acid and at the same concentration of a salt is practically constant, when the concentration of the latter does not exceed ·1 *N*. But it decreases in the order Cl>Br>I for the normal concentration (1·83, 1·76, 1·46).

It would thus appear that specific effects are at work. Broadly speaking, the results point to the conclusion that each of these salt-solutions should be treated as a separate solvent. At very low ionic strengths, the solutions can be treated as being identical and the limiting dissociation constant would appear to be about $8{\cdot}5 \times 10^{-3}$. On passing from ·1 *N* to 1.0 *N* concentration, the change in the value of the constant is remarkable ; it increases five times in some cases. Apart from a recognition of the specific solvent properties of each salt concentration, reference may be made to two other possible reasons for these variations. These are as follows :—

(*i*) The activity coefficients used in calculating the concentrations of the undissociated acid and the method of calculation itself are not valid. It is difficult however to account for the wide variations from such considerations.

(*ii*) The other possibility is that the activity of the hydrogen ions is not equal to that of the univalent $H_2PO_4^-$ ions. This inequality may arise from a difference in their concentrations. The second and third dissociation constants of phosphoric acid are given by Prideaux and Ward (*loc. cit.*) to be equal to 6×10^{-8} and $1{\cdot}1 \times 10^{-12}$ respectively and as has been stated before, these stages of dissociation may be neglected. The possibility remains however that certain amount of anions containing potassium may be formed. This would have the effect of lowering the concentration of $H_2PO_4^-$ ions. This would increase with the concentration of the salt.

Further experiments in the light of the above points are in progress.

My grateful thanks are due to Prof. J. N. Mukherjee for suggesting this work and for advice and facilities for conducting this work in his laboratory.

PHYSICAL CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
CALCUTTA.

Received March 7, 1931.

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part X. The Rotatory Dispersion of Stereoisomeric Phenyl and Iodophenyl Derivatives of Iminocamphors and Aminocamphors.*

By Bawa Kartar Singh, Hariprasad Basu-Mallik, and (in part) Bhutnath Bhaduri.

The relation between chemical constitution and rotatory power which is investigated in the present paper is that of position isomerism and rotatory dispersion in the aryl derivatives of iminocamphors and aminocamphors, the former being obtained by the condensation of the three stereoisomeric camphorquinones (*d*, *l*, *dl*) with aniline and iodoaniline (*o*, *m*, *p*), and the latter from the former by reduction.

$$C_8H_{14}\begin{cases}C{=}N\cdot R\\ |\\ CO\end{cases} \xrightarrow{H_2} C_8H_{14}\begin{cases}CH\cdot NHR\\ |\\ CO\end{cases}$$

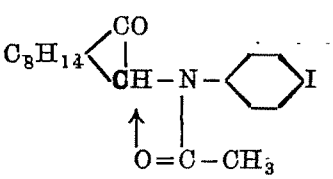
o-Iodoaniline and *d*-camphorquinone are found to give three forms of *o*-iodophenyliminocamphor melting at 86° (α), 93° (β) and 97° (γ) respectively according to the temperature of reaction and the process of crystallisation (*vide* Experimental). The conversion of the α-form into the γ- form with or without a trace of the latter and that of the β-form into the γ- modification only in the presence of a trace of the γ-form by heat show that these forms are three distinct substances and not impure specimens of one and the same substance. This is also borne out by their analytical data and the identical values of their rotatory power in different solvents (Table III).

These forms are shown to be polymorphic by the method developed by one of us (Singh, *J. Indian Chem. Soc.*, 1929, **6**, 1007), which is based on the determination of their dispersion. The values of

* This work was originally undertaken jointly with Messrs. Mahan Singh and Raghunath Rai, but before it had advanced appreciably this collaboration ceased on account of their having left this laboratory.

rotatory dispersion are identical for polymorphous modifications, whereas the values are different for isomeric (or tautomeric) modifications.

Some interesting examples of the influence of substituents on the course of a reaction were encountered in dealing with the stereoisomeric *o*-iodophenylaminocamphors. It was found that no hydrochlorides were produced by saturating their ethereal solutions with hydrogen chloride. The *meta* and *para* isomerides readily yielded hydrochlorides under this treatment. In this respect the behaviour is similar to that of 2:4:6-trichloro-3-iodoaniline which also does not give the hydrochloride by saturating its alcoholic solution with hydrogen chloride (McCombie and Ward, *J. Chem. Soc.*, 1913, **103**, 1995). The inhibitive action of the two *ortho* substituents on the production of a derivative is also seen in the halogen substituted phenols (Brazier and McCombie, *J. Chem. Soc.*, 1912, **101**, 968). The results are quite satisfactory when one at least of the *ortho* positions relative to the hydroxyl groups is unsubstituted. The failure to form a hydrochloride met with *o*-iodophenylaminocamphor in which one of the *ortho*-positions is free, must be, therefore, attributed to the steric hindrance reinforced by the camphoryl group replacing one of the hydrogen atoms of the amino-group. The sign of the rotatory power of *p*-iodophenylaminocamphors is reversed when the bases are converted into their acetyl derivatives: +89·64° to −23·49° for $[\alpha]_{Hg(green)}$ (in chloroform). A similar reversal of sign on acetylation has been observed already in the case of *p*-phenylene-bisaminocamphor (Singh and Bhaduri, *J. Indian Chem. Soc.*, 1930, 7, 545). The reversal of the sign of rotatory power in the latter example was explained and corelated with the saturation of a lone pair of electrons on the acyl oxygen and a similar explanation seems feasible in the present case and is shown in the following formula by the postulation of a " dative bond " (Menzies, *Nature*, 1928, **121**, 457) between the acyl oxygen atom and the hydrogen atom attached to the asymmetric carbon atom (C).



(I)

This reversal of sign of rotatory power is exhibited in the graphs of rotatory dispersion of the *dextro-* and *laevo-*isomerides (Fig. I).

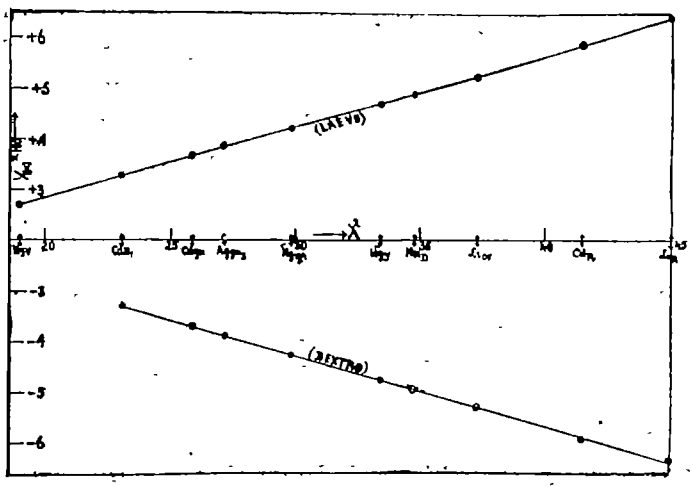


FIG. 1.

Rotatory dispersion of acetyl derivative of p*-iodophenylaminocamphor* (d & l).

The reversal of sign of rotatory power of a derivative may also be explained from the polarity of the substituents. The optical activity of the parent amino-compound may be regarded as being largely governed by the secondary amino-group which is attached to the asymmetric carbon atom. This group is of the electropositive or electron-repelling type; its optical influence (positive rotation) will be increased by the introduction of another group of the same character, and diminished (and even reversed in sign) by the introduction of a group of the opposite polar character, such as acyl group and is shown in the following scheme (the direction of electron shift being indicated by an arrow):

$$R-NH_2 \qquad\qquad R{\cdot}NH{\cdot}CO{\cdot}CH_3$$

The Influence of Solvent on the Rotatory Power.—The solvents employed in this work in the decreasing order of their dielectric constants are methyl alcohol > ethyl alcohol > acetone > chloroform > ether > benzene. A reference to tables of rotatory power will

show that the sequence of solvents in order of decreasing (or increasing) rotatory power is quite different from that of their dielectric constants. The rotatory power of the derivatives of phenyliminocamphor is highest in benzene (with a slight deviation in the case of *o*-iodophenyliminocamphor) which has the lowest dielectric constant, but this regularity does not extend to the derivatives of phenylaminocamphor (Table A). The rotatory power of all the compounds is lower in methyl alcohol than in ethyl alcohol, whereas the order of their dielectric constants runs in the opposite direction. The rotatory power of a compound does not bear any simple relation to the dielectric constant of the solvent in which it is dissolved is evident from the rotation values of phenylaminocamphor and its derivatives in chloroform (Table A). The rotatory powers are highest in chloroform with a slight deviation in the case of the *meta*-compound, whereas the value of dielectric constant stands intermediate in the series.

The Influence of Position and Nature of the Substituent on the Rotatory Power.—The order of the rotarory power of the derivatives of phenyliminocamphor in the six solvents is *p*>*unsubstituted* >*m*>*o*, whereas in the case of derivatives of phenylaminocamphor this order is *m*>*unsubstituted* >*p*>*o* (Table A). The order predicted from Frankland's "lever arm" theory (Frankland and Wharton, *J. Chem. Soc.*, 1896, **69**, 1583), namely, *p*>*m*> *unsubstituted* >*o*, is followed in the derivatives of phenyliminocamphor, except for the inverted relationship of the *meta*- and the *unsubstituted* compound. This regularity disappears in the derivatives of phenylaminocamphor in which the observed order *m* > *unsubstituted* >*p*>*o* does not agree with this theory. The rule of Cohen (Cohen and Dudley, *J. Chem. Soc.*, 1910, **97**, 1738 ; Cohen, *ibid*, 1911, **99**, 1058) which states that the rotatory effect of the *ortho*-grouping differs more from that of the phenyl than do those of *meta*- and *para*-groupings, is followed in both the series. The conception of a mechanical moment in the "lever arm" theory of Frankland is being replaced by that of an electrostatic moment. The introduction of a polar group into a hydrocarbon molecule is compared to the insertion of an electrostatic doublet, which according to the nature of the substituent may be oriented with either its positive or negative end towards the parent molecule (Thomson, *Phil. Mag.*, 1923, [*vi*], **46**, 497). Thomson has discussed the problem from a theoretical

TABLE A.

Name of the compound.	Benzene. (2·28)*	Ether. (4·3)	Chloroform. (5·2)	Acetone. (21·5)	Ethyl alcohol. (25·8)	Methyl alcohol. (31·2)
Phenyliminocamphor.	2192°	1925°	2153°	1963°	2007°	1940°
o-Iodophenyliminocamphor.	1093	863·5	983	1110	907·9	915
m-Iodophenyliminocamphor.	1907	1602	1771	1664	1710	1650
p-Iodophenyliminocamphor.	2462	2080	2380	2122	2193	2164
	The order of rotatory power: $p > unsubstituted > m > o$					
Phenylaminocamphor.	337·3	336·4	355·3	307·2	293·2	277·1
o-Iodophenylaminocamphor.	163·8	238·5	285·1	224·2	209·7	183·1
m-Iodophenylaminocamphor.	405·1	418·9	405·0	323·1	318·9	299·8
p-Iodophenylaminocamphor.	316·2	307·9	330·2	298·4	266·2	262·8
	The order of rotatory power.: $m > unsubstituted > p > o$					

* Dielectric constant is given within brackets below the names of the solvents.

standpoint, and concludes that with two substituents of similar polarity, the electrostatic moments should be in the order $o >$ *m*, *unsubstituted* nucleus $> p$, and with two substituents of opposite polarity in the order $p >$ *m*, *unsubstituted* $> o$. If the conception of mechanical moment is replaced by that of an electrostatic moment, the influence of a substituent on the optical rotation of a parent compound will be dependent in sign and magnitude on the change in electrostatic moment, and will either be of the order $p > m > o$, or, $o > m > p$, and not in the former sequence alone as required by the suggestion of Frankland. The agreement between the experimental and the predicted order is exact in the case of derivatives of phenyliminocamphor, but the displacement of *meta* and the *unsubstituted* compounds in the derivatives of phenylaminocamphor cannot be accounted for.

The Influence of Chemical Constitution on the Rotatory Dispersion.—The substances investigated in the present paper show two types of rotatory dispersion, namely, "simple" and "complex." Phenyliminocamphor shows simple rotatory dispersion in all the solvents (except ethyl alcohol), whereas phenylaminocamphor exhibits complex rotatory dispersion (Tables I and II). *o*-Iodophenyliminocamphor shows simple dispersion in two solvents only namely, methyl alcohol and benzene, but its reduction product, *o*-iodophenylaminocamphor, possesses simple rotatory disperson in all the solvents (Tables III and IV). The *meta*- and *para*-isomerides of both the series give simple rotatory dispersion in some solvents, and complex rotatory dispersion in others (Tables V to VIII). The rotatory dispersion of camphorquinones is simple in all the solvents (Table X ; compare also Lowry and Cutter, *J. Chem. Soc.*, 1925, **127**, 604). It is thus clear from the analysis of the above mentioned compounds that the type of roatory dispersion which a substance exhibits depends also on the nature of the solvent in which it is dissolved. The acetyl derivatives of *p*-iodophenylaminocamphors are interesting as they seem to obey exactly Biot's law of inverse squares, $[\alpha] = k/\lambda^2$ (Table IX). Experience hitherto has shown that this law was never obeyed exactly, although some substances such as sodium tartrate (Lowry and Austin, *Phil. Trans.*, 1922, A, **222**, 249) and octyl oxalate (Lowry and Richards, *J. Chem. Soc.*, 1924, **125**, 1593) obey it very nearly.

The Physical Identity of Enantiomers.—In Parts VIII and IX of this series of investigations, it has been shown that the rotatory

power of the *dextro*- and *laevo*-enantiomers is identical in magnitude. The values of rotatory power recorded in Tables I to X further support Pasteur's fundamental principle of molecular dissymmetry according to which the *d*- and *l*-forms are represented as true mirror images of one another, differing in sign but absolutely identical in the numerical magnitude of the rotatory power.

The melting points of the inactive forms in both the series (with the exception of the *ortho*-isomerides) are higher than those of the active isomers. This shows that the inactive forms in those cases are, in the solid state, true racemates.

Experimental.

o-*Iodophenylimino*-d-*camphor*.

There are three polymorphic modifications of this substance: α (m.p. 87°), β (m.p. 93°) and γ (m. p. 97°).

β-Modification, m. p. 93°.—Molecular proportions of *o*-iodoaniline and *d*-camphorquinone were mixed together with two or three times the weight of anhydrous sodium sulphate and the mixture heated at 90—97° for about four hours. The substance was extracted with alcohol and on the addition of water an oil came down. The oil on being repeatedly dissolved in alcohol and reprecipitated with water, solidified to a yellow substance. It was recrystallised as yellow prisms (m. p. 93°) by dissolving it in the least possible quantity of hot alcohol and stirring the solution during cooling. (Found: C, 52·31, 52·17; H, 4·99, 5·22. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.).

α-Modification, m. p. 86-87°.—The lowest melting form is obtained on condensing *d*-camphorquinone and *o*-iodoaniline in molecular proportions in the presence of anhydrous sodium sulphate at 80—85°. The product of condensation is extracted with hot alcohol, the solution cooled *undisturbed* in an ice-bath, when light yellow prisms, m. p. 87°, are deposited. It is extremely soluble in chloroform, readily soluble in carbon disulphide, less so in ether, glacial acetic acid and benzene, still less in acetone, sparingly soluble in ethyl alcohol and methyl alcohol and insoluble in water. (Found: C, 52·01; 52·02; H, 4·93; 4·83. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.).

γ-Modification, m. p. 97°.—The highest melting form is obtained when a saturated alcoholic solution of the form, m. p. 87°, is boiled

for a few minutes, cooled and precipitated with water. It is deposited as yellow prisms, m. p. 97°. It is, however, more conveniently obtained by heating for a few minutes the α-form or for a longer period the intermediate melting form (β) at 75—80° with a trace of the highest melting form (obtained from a previous operation), or by heating the α-form alone near its melting point for a longer period. (Found: C, 52·24, 52·13; H, 5·35; 5·25. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.). The rotatory powers of the three forms are recorded in (Table III).

o-*Iodophenylimino*-l-*camphor* was prepared in a similar way as the corresponding *dextro*-isomeride but was isolated in one modification only, namely, that melting at 93°. (Found: C, 52·13; H, 5·25. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.). The rotatory power in different solvents is identical with that of *d*-isomeride (Table III).

o-*Iodophenylimino*-dl-*camphor* was obtained in a similar way as its optically active isomerides and recrystallised out of alcohol as long yellow rectangular prisms melting at 85°. It had similar solubility in organic media as the optically active forms. (Found: C, 52·0; H, 5·11. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.).

o-*Iodophenylamino*-d-*camphor* was prepared in the usual way by the reduction of the three polymorphic modifications of o-iodophenylimino-*d*-camphor described above (in ether solution) with 10% potassium hydroxide solution and zinc dust, and was thrice crystallised out of alcohol as flat transparent prisms melting at 147—48°. The mixed melting point of the specimens obtained from the three polymorphic modifications was also 147—48° showing that all of them are one and the same compound.

It is extremely soluble in ether and chloroform, readily soluble in carbon disulphide and benzene, less so in acetone, fairly soluble in methyl alcohol and ethyl alcohol and insoluble in water. (Found: C, 52·48 ; H, 5·51. $C_{16}H_{20}ONI$ requires C, 51·08; H, 5·44 per cent). The order of rotatory power in different solvents (Table IV) is as:—

Chloroform > ether > acetone > ethyl alcohol > methyl alcohol > benzene.

o-Iodophenylamino-*d*-camphor does not yield a hydrochloride when its ethereal solution is saturated with hydrochloric acid gas.

o-*Iodophenylamino*-l-*camphor* was obtained in the usual way as colourless prisms melting at 148°. It had the same solubility as its *d*-isomeride. (Found: C, 51·99; H, 5·64. $C_{16}H_{20}ONI$ requires C, 52·03; H, 5·42 per cent.). The rotatory power is identical with with that of the *d*-isomeride (Table IV). The *l*-base also does not yield the hydrochloride.

o-*Iodophenylamino*-dl-*camphor* was obtained in the usual way as its two optically active isomerides, as rectangular plates melting at 144-45°. (Found: C, 51·96; H, 5·59. $C_{16}H_{20}ONI$ requires C, 52·03 ; H, 5·42 per cent.). The *dl*-base, like its optically active isomerides, does not yield a hydrochloride.

m-*Iodophenylimino*-d-*camphor*.—This substance was obtained by heating *d*-camphorquinone and *m*-iodoaniline (in molecular proportions) together with an excess of anhydrous sodium sulphate in the usual way, as yellow prisms melting at 112-13°. The solubility of this substance in different solvents is of the same order as that of its *ortho*-isomeride. (Found: C, 52·18; H, 5·12. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.). The order of rotatory power in different solvents (Table V) is:

Benzene > chloroform > ethyl alcohol > acetone > methyl alcohol > ether.

The *l*-isomeride was prepared in a similar way from *l*-camphorquinone and has the same melting point and solubility as the *d*-isomeride. (Found: C, 52·20; H, 5·33. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.). The rotatory power is identical with that of the *d*-isomeride (Table V).

m-*Iodophenylimino*-dl-*camphor* was prepared in the same way as the optically active isomerides, and was crystallised out of 70 per cent alcohol as light yellow prisms melting at 116°. It is readily soluble in chloroform, benzene and acetone ; less so in ether, moderately soluble in methyl alcohol and ethyl alcohol and insoluble in water. (Found: C, 52·07 ; H, 5·05. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.).

m-*Iodophenylamino*-d-*camphor*.—This was prepared in the usual way by the reduction of *m*-iodophenylimino-*d*-camphor and was obtained as prismatic needles melting at 109—110°. Its solubility in different solvents is in the same order as that of the *ortho*-isomeride. (Found: C, 51·75 ; H, 5·85. $C_{16}H_{20}ONI$ requires C, 52·03 ; H, 5·42 per cent). The order of rotatory power in different solvents (Table VI) is as ether > benzene > chloroform > acetone >

ethyl alcohol>methyl alcohol. The *hydrochloride* of the above base was prepared by saturating its ethereal solution with dry hydrochloric acid gas. (Found: Cl, 8·68. $C_{16}H_{21}ONICl$ requires Cl, 8·64 per cent.). Water decomposes the hydrochloride into the original base and free hydrochloric acid.

m-*Iodophenylamino*-l-*camphor* was prepared in a similar way as the corresponding *d*-isomeride and has the same melting point and solubility. (Found: C, 52·07 ; H, 5·94. $C_{16}H_{20}ONI$ requires C, 52·03 ; H, 5·42 per cent.). The magnitude of the rotatory power is identical with that of the *d*-compound (Table VI). The hydrochloride of the *l*-base was prepared in the same way as that of the *d*-isomeride and has similar properties. (Found: Cl, 8·53. $C_{16}H_{21}ONClI$ requires Cl, 8·64 per cent.).

m-*Iodophenylamino*-dl-*camphor* was prepared in a similar way as its two optically active isomeride and crystallised as transparent rectangular prisms melting at 123°. It is very readily soluble in acetone, benzene, and chloroform, less so in ether, sparingly soluble in methyl alcohol and ethyl alcohol and insoluble in water. (Found: C, 51·83 ; H, 5·55. $C_{16}H_{20}ONI$ requires C, 52·03 ; H, 5·42 per cent.). m-*Iodophenylamino*-dl-*camphor hydrochloride* prepared in the usual way, melted at 162°. (Found: Cl, 8·32. $C_{16}H_{21}ONICl$ requires Cl, 8·64 per cent.).

p-*Iodophenylimino*-d-*camphor* was obtained from *d*-camphorquinone and *p*-iodoaniline (molecular proportions) in the usual way and was recrystallised from 80% alcohol as flat prisms melting at 113-114°. It is extremely soluble in chloroform, less so in carbon disulphide, ether, glacial acetic acid, benzene and acetone, sparingly soluble in methyl alcohol and ethyl alcohol and insoluble in water. (Found: C, 52·33; H, 4·91; N, 4·07. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91; N, 3·80 per cent.). The order of rotatory power in different solvents (Table VII) is benzene>chloroform>ethyl alcohol>methyl alcohol>acetone>ether.

The *l*-isomeride was prepared in a similar way and has the same melting point and solubility. (Found: C, 52·22; H, 5·41. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.). The rotatory power is identical with that of the *d*-isomeride (Table VII).

p-*Iodophenylimino*-dl-*camphor*, prepared in a similar way as the corresponding *d*- and *l*-compounds, was recrystallised out of 70% alcohol as yellow rectangular prisms melting at 132°. It is readily soluble in acetone, benzene and chloroform, less so in ether, methyl

alcohol and ethyl alcohol and insoluble in water. (Found: C, 52·13; H, 4·90. $C_{16}H_{18}ONI$ requires C, 52·31; H, 4·91 per cent.).

p-*Iodophenylamino*-d-*camphor* was prepared from *p*-iodophenylimino-*d*-camphor in the same way as the other two position isomerides and was obtained as flat prisms melting at 113-14°. It is extremely soluble in ether and chloroform, readily soluble in carbon disulphide and benzene, fairly soluble in acetone, methyl alcohol and ethyl alcohol and insoluble in water. (Found: C, 51·91; H, 5·47. $C_{16}H_{20}ONI$ requires C, 52·03; H, 5·42 per cent.). The order of rotatory power in solvents (Table VIII) is chloroform>benzene>ether>acetone>ethyl alcohol>methyl alcohol. The *hydrochloride* was obtained in the usual way as fine colourless needles melting at 125-26°. (Found: Cl, 8·14. $C_{16}H_{20}ONI$, HCl requires Cl, 8·64 per cent). It is resolved into hydrochloric acid and the free base by the addition of water.

p-*Iodophenylamino*-l-*camphor* was prepared (from *l*-camphorquinone) in the same way as the corresponding *d*-isomeride and has the same melting point and solubility. (Found: C, 51·93; H, 5·64. $C_{16}H_{20}ONI$ requires C, 52·03; H, 5·42 per cent.). The rotatory power is identical with that of the *d*-isomeride within experimental error (Table VIII). p-*Iodophenylamino*-l-*camphor hydrochloride* was prepared in the usual way. (Found: Cl, 8·28. $C_{16}H_{20}ONI$, HCl requires Cl, 8·64 per cent.).

p-*Iodophenylamino*-dl-*camphor* was prepared in the same way as the corresponding *d*- and *l*-compound, and was crystallised out of alcohol as transparent prisms melting at 160°. It is very readily soluble in chloroform, benzene, and acetone, less so in ether, somewhat sparingly soluble in methyl alcohol and ethyl alcohol and insoluble in water. (Found: C, 52·06; H, 5·59. $C_{16}H_{20}ONI$ requires C, 52·03; H, 5·42 per cent.). The *hydrochloride* obtained by saturating an ethereal solution of the base with hydrochloric acid gas melted at 127°. (Found: Cl, 18·41. $C_{16}H_{20}ONICl$ requires Cl, 8·64 per cent.).

The *acetyl* derivative of *p*-iodophenylamino-*d*-camphor was prepared by heating *p*-iodophenylamino-*d*-camphor (1 g.) with acetic anhydride (1·2 g.) at 160° for one hour and obtained as hexagonal plates, melting at 117-118° (yield 50 per cent.). It is freely soluble in the ordinary organic media. (Found: C, 52·39; H, 5·62. $C_{18}H_{22}O_2NI$ requires C, 52·56; H, 5·35 per cent.).

The rotatory power was observed in chloroform and is recorded in Table IX.

The *l*-iso meride was prepared in a similar way from *p*-iodophenylamino-*l*-camphor and has the same melting point and solubility. (Found: C, 52·26; H, 5·62. $C_{18}H_{22}O_2NI$ requires C, 52·56; H, 5·35 per cent.). The rotatory power is identical in numerical value with that of the *d*-isomeride (Table IX).

Phenylimino-l-*camphor.*—*l*-Camphorquinone and aniline in molecular proportions were heated together in the presence of fused anhydrous sodium sulphate on the water-bath till the product on cooling became a hard mass. It was crystallised out of alcohol as long yellow needles melting at 107-108°. It is readily soluble in acetone, chloroform and benzene; less so in ether, methyl alcohol, ethyl alcohol and petroleum ether and insoluble in water. (Found: C, 79·78; H, 8·15. $C_{16}H_{19}ON$ requires C, 79·68; H, 7·88 per cent.). The rotatory power of the *dextro-* and *laevo-* compounds are identical (Table I).

Phenylimino-dl-*camphor*, prepared from *dl*-camphorquinone in the same way as the *laevo*-isomeride, after recrystallisation from 60 per cent. alcohol, as yellow prismatic needles, melted at 124°. (Found: N, 5·95. $C_{16}H_{19}ON$ requires N, 5·81 per cent.)

Phenylamino-l-*camphor.*—This was prepared in the usual way by the reduction of phenylimino-*l*-camphor and was crystallised as flat transparent prisms melting at 80°. It is readily soluble in benzene, chloroform, and ether, sparingly soluble in methyl alcohol, and ethyl alcohol, still less so in petroleum ether and insoluble in water. (Found: C, 79·04; H, 8·89. $C_{16}H_{21}ON$ requires C, 79·01; H, 8·64 per cent.).

The rotatory power of the *dextro-* and *laevo*-isomerides are equal in magnitude and the order in different solvents (Table II) is as chloroform > benzene > ether > acetone, ethyl alcohol > methyl alcohol.

The dextro-*hydrochloride* obtained in the usual way from the *d*-base melts at 175°. (Found: Cl, 12·56. $C_{16}H_{21}ON,HCl$ requires Cl, 12·70 per cent.).

The laevo-*salt* also melts at 175°. (Found: Cl, 12·70. $C_{16}H_{21}ON,HCl$, requires Cl, 12·70 per cent.).

Phenylamino-dl-*camphor*, prepared in the usual way, by the reduction of phenylimino-*dl*-camphor, was recrystallised out of hot alcohol as colourless plates melting at 104-105°. (Found: C, 78·96; H, 8·52; N, 5·83. $C_{16}H_{21}ON$ requires C, 79·00; H, 8·64; N, 5·76 per cent.).

The *hydrochloride* was obtained by saturating the ethereal solution of *dl*-phenylaminocamphor with hydrochloric acid gas as a white precipitate melting at 170—171°. (Found: N, 5·26. $C_{16}H_{21}ON$, HCl requires N, 5·21 per cent.).

The rotatory power determinations were made in a 2-dcm. jacketed tube at 35°. $Hg_{vio.}$, $Hg_{gr.}$, $Hg_{yel.}$ and Na_D refer to the violet mercury line 4358, the green mercury line 5461, the yellow mercury line 5780, and the sodium line 5893 respectively. The value of λ_0, calculated from the dispersion formula is given in the tables, and is expressed as μ or 10^{-4} cm.

TABLE I.

Phenyliminocamphor.

Solvent.	Concentration: g/100 c.c.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Ether	$[\alpha]=\frac{110{\cdot}69}{\lambda^2-0{\cdot}1595}$; [M]=2·41 [α]; $\lambda_0=0{\cdot}3994_4$			
Dextro	0·7148	+1424°	+1526°	+1927°
Lævo	0·7068	−1420	−1524	−1923
Mean (obs.)		1422	1525	1925
Calc.		1424	1528	1923
Diff.		−2	−3	+2
Methyl alcohol	$[\alpha]=\frac{110{\cdot}08}{\lambda^2-0{\cdot}1621}$; [M]=2·41 [α]; $\lambda_0=0{\cdot}4026$.			
Dextro	0·6864	+1436	+1546	+1941
Lævo	0·6820	−1442	−1547	−1938
Mean (obs.)		1439	1547	1940
Calc.		1432	1543	1949
Diff.		+7	+4	−9
Acetone	$[\alpha]=\frac{117{\cdot}11}{\lambda^2-0{\cdot}1548}$; [M]=2·41[α]; $\lambda_0=0{\cdot}3928$.			
Dextro	0·6992	+1462°	+1570°	+1964°
Lævo	0·6952	−1455	−1567	−1961
Mean (obs.).		1459	1569	1963
Calc.		1462	1570	1961
Diff.		−3	−1	+2

Solvent.	Concentration : g/100 c.c.		[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Chloroform $[\alpha]=\frac{125{\cdot}56}{\lambda^2-0{\cdot}1576}$; $[M]=2{\cdot}41[\alpha]$; $\lambda_0=0{\cdot}3970$.					
Dextro	0·6972		+1597°	+1716°	+2153°
Laevo	0·4964		−1590	−1716	−2153
Mean (obs.).			1594	1716	2153
Calc.			1596	1715	2153
Diff.			−2	+1	+0
Benzene $[\alpha]=\frac{126{\cdot}15}{\lambda^2-0{\cdot}1595}$; $[M]=2{\cdot}41[\alpha]$; $\lambda_0=0{\cdot}3994$.					
Dextro	0·7124		+1622	+1741	+2195
Laevo	0·6876		−1621	−1735	−2189
Mean (obs.)			1622	1738	2192
Calc.			1619	1741	2192
Diff.			+3	−3	+0
Ethyl alcohol	0·6944	*d*	+1489	+1605	+2009
	0·7100	*l*	−1494	−1608	−2004
		mean	1492	1604	2007

TABLE II.

Phenylaminocamphor.

Solvent.	Concentration : g/100 c.c.	Dextro, laevo, or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$	[M] $Hg_{vio.}$
Methyl alcohol	0·6096	*d*	+235·3°	+243·2°	+277·1°	+492·3°
	0·5572	*l*	−233·3	−241·9	−277·1	−497·1
		mean	234·3	242·5	277·1	494·7
Ethyl alcohol	0·6140	*d*	+263·2	+267·1	+298·8	+526·4
	0·5512	*l*	−257·9	−266·8	−297·6	−530·4
		mean	260·6	267·0	298·2	528·4
		d	+265·1	+269·2	+305·6	+590·9
Acetone	0·6004	*l*	−261·8	−266·3	−308·7	−596·9
	0·5476	mean	263·5	267·8	307·2	593·9
Ether	0·6036	*d*	+282·1	+293·9	+336·1	+672·2
	0·5524	*l*	−280·9	−290·3	−336·7	−673·5
		mean	281·5	292·1	336·4	672·6
Benzene	0·6064	*d*	+289·6	+295·6	+337·5	+681·1
	0·5524	*l*	−282·6	−291·6	−337·0	−689·5
		mean	286·1	293·6	337·3	685·3
Chloroform	0·6080	*d*	+299·7	+305·9	+335·7	+705·5
	0·6128	*l*	−293·4	−301·3	−354·9	−701·8
		mean	296·6	303·6	355·8	703·7

TABLE III.

o-Iodophenyliminocamphor.

Solvent.	Concentration : g/100 c.c.	Dextro, laevo, or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
	0·6780	*d*	+633·3°	+703·7°	+863·4°
Ether	0·6716	*l*	−639·5	−707·8	−863·6
		mean	636·4	705·8	863·5
	0·6700	*d*	+663·0	+736·9	+903·8
Ethyl alcohol	0·6760	*l*	−656·9	−743·9	−912·0
		mean	660·0	740·4	907·9
(α)	0·7204	*d*	+748·7	+781·8	+976·0
Chloroform (β)	0·7200	*d*	+762·0	+795·4	+989·2
(γ)	0·7228	*d*	+758·7	+789·3	+985·2
	0·6756	*d*	+771·4	+896·4	+1106
Acetone	0·6612	*l*	−779·8	−904·6	−1113
		mean	775·6	900·5	1110
Methyl alcohol $[\alpha]=\frac{36{\cdot}72}{\lambda^2-0{\cdot}1446}$; $[M]=3{\cdot}67[\alpha]$; $\lambda_0=0{\cdot}3803$.					
(γ) m.p. 96°-67°	0·7220	*d*(obs.)	+693·8°	+739·8°	+915·0
Calc.			693·8	741·4	914·9
Diff.			±0	−1·6	+0·1
(β) m.p. 93°	0·7200	*d*(obs.)	+693·5	+736·5	+915·0
Calc.			693·8	741·4	914·9
Diff.			−0·3	−4·9	+0·1
(α) m.p. 86°-87°	0·7228	*d*(obs.)	+690·9	+736·5	+914·2
Calc.			693·8	741·4	914·
Diff.			−2·9	−4·9	−0·7
Benzene $[\alpha]=\frac{41{\cdot}38}{\lambda^2-0{\cdot}1596}$; $[M]=3{\cdot}67[\alpha]$; $\lambda_0=0{\cdot}3995$.					
(γ) m.p. 96°-97°	0·4860	*d*(obs.)	+808·2°	+864·8	+1095·0
Calc.			809·9	870·5	1095·0
Diff.			−1·7	−5·7	0
(β) m.p. 93°	0·7282	*d*(obs.)	+809·8	+870·6	+1093·5
Calc.			809·9	870·5	1095·0
Diff.			−0·1	+0·1	−1·5
(α) m.p. 86°-87°	0·7244	*d*(obs.)	+810·6	+869·2	+1092·0
Calc.			809·9	870·5	1095·0
Diff.			+0·7	−1·3	−3·0

TABLE IV.

o-Iodophenylaminocamphor.

Solvent.	Concentration : g/100 c.c.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$	[M] $Hg_{vio.}$
Benzene $[\alpha]=\frac{9'79}{\lambda^2-0{\cdot}0762}$; $[M]=3{\cdot}69\,[\alpha]$; $\lambda_0=0{\cdot}2760$.					
Dextro (obs.)	0°6648	+133·2°	+141·6°	+163·8°	+316·4°
Calc.		133·4	140·1	162·8	317·5
Diff.		−0·2	+1·5	+1·0	−1·1
Methyl alcohol $[\alpha]=\frac{12{\cdot}02}{\lambda^2-0{\cdot}0554}$; $[M]=3{\cdot}69\,[\alpha]$; $\lambda_0=0{\cdot}2354$.					
Dextro (obs.)	0·6542	+152·1	+157·7	+183·1	+329·5
Calc.		152·25	159·2	182·8	329·7
Diff.		−0·15	−1·5	+0·3	−0·2
Ethyl alcohol $[\alpha]=\frac{13'74}{\lambda^2-0{\cdot}0544}$; $[M]=3{\cdot}69\,[\alpha]$; $\lambda_0=0{\cdot}2332$.					
Dextro	0·6596	+173·45	+181·8	+209·75	+385·9
Laevo	0·2560	−173·0	−180·1	−209·0	−360·25
Mean (obs.)		173·2	181·0	209·4	373·8
Calc.		173·3	181·3	208·0	374·0
Diff.		−0·1	−0·2	+1·4	+0·2
Acetone $[\alpha]=\frac{14{\cdot}62}{\lambda^2-0{\cdot}0581}$; $[M]=3{\cdot}69\,[\alpha]$; $\lambda_0=0{\cdot}2410$.					
Dextro	0·6654	+188·2	+196·55	+224·25	+412·4
Laevo	0·6592	−184·7	−195·9	−221·1	−404·1
Mean (obs.)		186·5	196·2	222·7	408·3
Calc.		186·6	195·4	224·6	409·0
Diff.		−0·1	+0·8	−1·9	−0·7
Ether $[\alpha]=\frac{14{\cdot}91}{\lambda^2-0{\cdot}0705}$; $[M]=3{\cdot}69[\alpha]$; $\lambda_0=0{\cdot}2655$.					
Dextro (obs.)	0·6652	+199·6	+208·0	+238·5	463·0
Calc.		198·85	208·6	241·5	+460·2
Diff.		+0·75	−0·6	−3·0	+2·8
Chloroform $[\alpha]=\frac{17{\cdot}73}{\lambda^2-0{\cdot}0675}$; $[M]=3{\cdot}69[\alpha]$; $\lambda_0=0{\cdot}2598$.					
Dextro	0·6676	+234·9	+246·1	+287·4	–
Laevo	0·6592	−232·3	−243·5	−282·7	−532·1
Mean (obs.)		233·6	244·8	285·1	532·1
Calc.		234·0	245·4	283·7	534·2
Diff.		−0·4	−0·6	+1·4	−2·1

TABLE V.

m-*Iodophenyliminocamphor*$_2$.

Solvent.	Concentration : g/100 c.c.	Dextro, leavo, or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Ether	0·6904	*d*	+1161°	+1284°	+1603°
	0·7156	*l*	−1164	−1279	−1601
		mean	1163	1282	1602
Acetone	0·6208	*d*	+1303	+1354	+1662
	0·6136	*l*	−1307	−1349	−1666
		mean	1305	1352	1664
Chloroform	0·6944	*d*	+1324	+1388	+1773
	0·6984	*l*	−1329	−1390	−1769
		mean	1327	1389	1771
Methyl alcohol	$[\alpha]=\frac{63\cdot95}{\lambda^2-0\cdot1561}$;	[M]=367[α];		$\lambda_0=0\cdot3951$	
Dextro	0·7376		+1229	+1319	+1652
Leavo	0·7304		−1231	−1321	−1648
Mean (obs.).			1230	1320	1650
Calc.			1229	1319	1652
Diff.			+1	+1	−2
Ethyl alcohol	$[\alpha]=\frac{71\cdot75}{\lambda^2-0\cdot1439}$	[M]=3·67[α];		$\lambda_0=0\cdot3793$.	
Dextro	0·7264		+1299	+1379	+1712
Leavo	0·7160		−1302	−1371	−1707
Mean (obs.).			1301	1375	1710
Calc.			1295	1384	1706
Diff.			+6	−9	+4
Benzene	$[\alpha]=\frac{74\cdot58}{\lambda^2-0\cdot1544}$;	[M]=3·67[α];		$\lambda_0=0\cdot3929$	
Dextro	0·7192		+1421	+1520	+1905
Leavo	0·7040		−1416	−1514	−1908
Mean (obs.)			1419	1517	1907
Calc.			1418	1522	1902
Diff.			+1	−5	+5

TABLE VI.

m-Iodophenylaminocamphor.

Solvent.	Concentration : g/100 c. c.	Dextro, laevo, or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$	[M] $Hg_{vio.}$
Acetone	0·7492	*d*	+244·0°	+290·8°	+325·4°	+586·7°
	0·6784	*l*	−252·8	−285·4	−320·8	−595·4
		mean	248·4	288·1	323·1	591·0
Chloroform	0·6500	*d*	+312·2	+351·9	+405·8	+817·4
	0·6860	*l*	−317·4	−349·5	−404·1	−814·7
		mean	314·8	351·7	405·0	186.1
Benzene	0·6816	*d*	+322·1	+341·1	+406·1	+833·9
	0·6848	*l*	−312·5	−344·8	−404·1	−824·3
		mean	317·3	343·0	405·1	829·1
Ether	0·6972	*d*	+330·8	+344·0	+420·8	+831·0
	0·6888	*l*	−329·5	−348·1	−416·9	−830·5
		mean	330·1	346·1	418·9	830·8

Methyl alcohol $[\alpha]=\frac{21{\cdot}28}{\lambda^2-0{\cdot}0392}$; $[M]=3{\cdot}69[\alpha]$; $\lambda_0=0{\cdot}1980$

Dextro	0·6456	+254·4	+265·8	+300·3	+520·2
Laevo	0·6904	−253·9	−264·5	−299·3	−526·5
Mean (obs.)		254·1	265·1	299.8	523·3
Calc.		255·0	266·25	303·15	520·7
Diff.		−0·9	−1·15	−3·35	+2·6

Ethyl alcohol $[\alpha]=\frac{19{\cdot}73}{\lambda^2-0{\cdot}0682}$; $[M]=3{\cdot}69[\alpha]$; $\lambda_0=0{\cdot}2612$

Dextro	0·7008	+263·2	+276·5	+318·9	+597·5
Laevo	0·6920	−258·7	−269·3	−314·7	−599·9
Mean (obs.).		261·0	272·9	316·8	598·7
Calc.		261·0	273·75	316·5	597·3
Diff.		±0	− 0·85	+0·3	+1·4

TABLE VII.

p-Iodophenyliminocamphor.

Solvent.	Concentration : g/100 c. c.	Dextro, levo, or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Ether	0·7072	*d*	+1517°	+1650°	+2081°
	0·6956	*l*	−1523	−1644	−2079
		mean	1520	1647	2080
Methyl alcohol	0·6676	*d*	+1575	+1721	+2166
	0·6936	*l*	−1580	−1720	−2162
		mean	1578	1721	2164
Acetone	0·7104	*d*	+1592	+1679	+2120
	0·6748	*l*	−1581	−1684	−2124
		mean	1587	1682	2122
Ethyl alcohol	$[\alpha]=\frac{84{\cdot}95}{\lambda^2-0{\cdot}1589}$;	$[M]=3{\cdot}67[\alpha]$;	$\lambda_0=0{\cdot}3986$.		
Dextro	0·6816		+1624	+1732	+2190
Lævo	0·6644		−1621	−1732	−2196
Mean (obs.)			1623	1732	2193
Calc.			1619	1740	2187
Diff.			+4	−8	+6
Chloroform	$[\alpha]=\frac{88{\cdot}88}{\lambda^2-0{\cdot}1613}$	$[M]=3{\cdot}67\,[\alpha]$;	$\lambda_0=0{\cdot}4016$.		
Dextro	0·6816		+1764	+1880	+2383
Lævo	0·6828		−1755	−1879	−2376
Mean (obs.)			1760	1880	2380
Calc.			1753	1888	2383
Diff.			+7	− 8	−3
Benzene	$[\alpha]=\frac{86{\cdot}51}{\lambda^2-0{\cdot}1691}$;	$[M]=3{\cdot}67\,[\alpha]$;	$\lambda_0=0{\cdot}4112$.		
Dextro	0·6780		+1781	+1927	+2462
Lævo	0·6660		−1772	−1923	−2461
Mean (obs.)			1777	1925	2462
Calc.			1782	1924	2459
Diff.			−5	+1	+3

TABLE VIII.

p-Iodophenylaminocamphor.

Solvent.	Concentration : g/100 c. c.	Dextro, levo or mean.	[M] Na_D	[M] $H_{yel.}$	[M] $Hg_{gr.}$	[M] $Hg_{vio.}$
Methyl alcohol	0·6824	*d*	+202·8°	+235·3°	+262·3°	+440·8°
	0·6800	*l*	−206·2	−233·8	−263·2	−444·8
		mean	204·5	234·3	262·8	442·6
Ethyl alcohol	0·6612	*d*	+214·8	+234·5	+267·9	+446·4
	0·6628	*l*	−206·0	−236·6	−264·4	−459·7
		mean	210·4	235·6	266·2	450·1
Acetone	0·6684	*d*	+242·9	+256·6	−300·8	+455·4
	0·6792	*l*	−244·4	−252·5	−296·0	−456·2
		mean	243·7	254·6	298·4	455·8
Benzene	0·6640	*d*	+241·7	+277·8	+313·9	+622·3
	0·6660	*l*	−249.3	−279·8	−318·5	−626·2
		mean	245·5	278·8	316·2	624·3

Ether $[\alpha]=\frac{18\cdot66}{\lambda^2-0\cdot0779}$; $[M]=3\cdot69\,[\alpha]$; $\lambda_0=0\cdot2791$.

Dextro	0·6624	+256·3	+272·9	+309·1	+615·8	
Laevo	0·6620	−250·8	−275·8	−306·6	−624·1	
Mean (obs.)			256·6	274·4	307·9	619·8
Calc.			256·3	269·3	313·2	615·4
Diff.			−2·7	+5·1	−5·3	+4·4

Chloroform $[\alpha]=\frac{21\cdot11}{\lambda^2-0\cdot0670}$; $[M]=3\cdot69[\alpha]$; $\lambda_0=0\cdot2588$.

Dextro	0·7140	+271·3	+284·2	+330·8	+643·3
Laevo	0·6604	−265·4	−282·1	−329·6	−642·4
Mean (obs.)		268·4	283·2	330·2	642·9
Calc.		278·0	291·6	337·0	633·8
Diff.		−9·6	−8·4	−6·8	+9·6

TABLE IX.

Acetyl Derivative of p-*Iodophenylaminocamphor.*

Solvent : *Chloroform* $[\alpha]=\frac{7{\cdot}017}{\lambda^2}$; $[M]=4{\cdot}11[\alpha]$

Dextro			Line.	Calc. $[\alpha]$	*Laevo*		
Concentration : g/100 c.c.	Obs. $[\alpha]$ $=o$.	$o-c$.		$=c$.	$o'-c$.	Obs. $[\alpha]$ $=o'$.	Concentration : g/100 c.c.
4·0016	—	—	Hg_{4358}	∓36·94°	−0·10	+36·84°	4·0020
	−30·36°	−0·09°	Cd_{4849}	30·45	+0·03	30·48	
	−27·17	+0·04	Cd_{5086}	27·13	−0·09	27·04	
	−25·86	±0·0	Ag_{5209}	25·86	−0·13	25·73	
	−23·49	−0·05	Hg_{5461}	23·54	+0·07	23·61	
	−21·00	−0·01	Hg_{5780}	21·01	+0·09	21·10	
	−20·24	+0·02	Na_{5893}	20·22	±0	20·23	
	−18·86	+0·03	Li_{6104}	18·83	+0·16	18·99	
	−16·87	−0·07	Cd_{6438}	16·94	−0·08	16·86	
	−15·74	+0·14	Li_{6708}	15·60	−0·01	15·61	

TABLE X.

Camphorquinone$_\varepsilon$

Solvent.	Concentration : g/100 c.c.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Benzene	$[\alpha]=\frac{13{\cdot}80}{\lambda^2-0{\cdot}2199}$;	$[M]=1{\cdot}66[\alpha]$;	$\lambda_0=0{\cdot}4689$.	
Dextro	1·0892	−180·4°	−198·9°	−293·9°
Laevo	1·0820	+181·2	+198·7	+293·5
Mean (obs.)		180·8	198·8	293·7
Calc.		180·0	200·5	292·4
Diff.		+0·8	−1·7	+1·3
Acetone	$[\alpha]=\frac{13{\cdot}78}{\lambda^2-0{\cdot}2200}$;	$[M]=1{\cdot}66[\alpha]$;	$\lambda_0=0{\cdot}4690$.	
Dextro	1·248	−180·7	−198·6	−293·6
Laevo	1·0192	+179·9	+197·8	+293·2
Mean (obs.		180·3	198·2	293·4
Calc.		179·4	199·7	291·5
Diff.		+0·9	−1·5	+1·9

TABLE X—(*contd.*).

Solvent.	Concentration : g/100 c.c.	[M] Na_D	[M] $Hg_{yel.}$	[M] Hg_{gr}
Chloroform	$[\alpha]=\frac{12.99}{\lambda^2-0.2294}$;	[M]=1·66[α];	$\lambda_0=0.4727$.	
Dextro	1·1520	−175·1	−193·9	−288·8
Laevo	1·1568	+173·8	+194·4	+288·5
Mean (obs.)		174·45	194·15	288·65
Calc.		174·8	194·8	288·2
Diff.		+0·15	−0·65	+0·45
Ether	$[\alpha]=\frac{12.15}{\lambda^2-0.2283}$;	[M]=1·66[α];	$\lambda_0=0.4778$	
Dextro	1·1356	−168·2	−190·4	−288·0
Laevo	1·1540	+170·5	+192·1	+287·3
Mean (obs.)		169·35	191·25	287·65
Calc.		169·5	190·6	288·5
Diff.		−0·15	+0·65	−0·86
Ethyl alcohol	$[\alpha]=\frac{12.08}{\lambda^2-0.2254}$;	[M] = 1·66 [α];	$\lambda_0=0.4748$.	
Dextro	1·1844	−164·7	−185·2	−274·8
Laevo	1·1776	+164·3	+184·1	+274·9
Mean (obs.)		164·5	184·65	274·85
Calc.		164·6	184·5	275·5
Diff.		−0·1	+0·15	−0·65
Methyl alcohol	$[\alpha]=\frac{7.98}{\lambda^2-0.2309}$;	[M] = 1·66[α];	$\lambda_0=0.4805$.	
Dextro	1·1692	−113·6	−129·2	−197·3
Laevo	1·1868	+113·9	+128·5	+195·9
Mean (obs.)		113·75	128·85	196·4
Calc.		113·8	128·4	196·75
Diff.		−0·05	+0·45	−0·35

We wish to make grateful acknowledgment to the Government of Bihar and Orissa in the Ministry of Education for the grant of research scholarships to two of us (H. B.-M. and B. B.) which have enabled them to take part in this investigation. We also wish to acknowledge the valuable assistance which we received from Babu Indramani Mahanti, B.Sc., the Head Assistant of the Chemical Department.

THE CHEMICAL LABORATORY,
RAVENSHAW COLLEGE, CUTTACK.

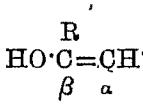
Received December 22, 1930.

β-Diketones in Ring Formation. Part III.

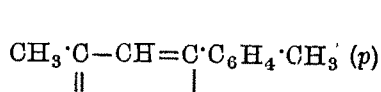
By Umaprasanna Basu.

In earlier parts of this work (Basu, *J. Indian Chem. Soc.*, 1930, 7, 482, 815) it has been shown that the methylene group of cyanoacetamide preferentially reacts with the enolic form of a β-diketone to give rise to a pyridone derivative, the yield depending on the nature of the β-substituent in the enolic ketone (I) as it generally governs the course of a Michael's reaction (*cf.* Cooper, Ingold and Ingold, *J. Chem. Soc.*, 1926, p. 1869).

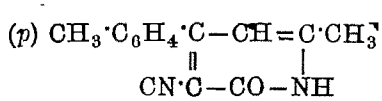
The condensation of *p*-toluoylacetone and ethyl benzoylpyruvate with cyanoacetamide has been studied in the present work and the evidence obtained suggests that in each case the yield of the different pyridone derivatives formed depends upon the β-substituent of the respective enolic ketone. When for instance, *p*-toluoylacetone was condensed with cyanoacetamide under the experimental conditions described later, the main product (more than 90% of the total yield) was a crystalline substance (II), the constitution of which was ascertained by its synthesis by other means (*vide infra*). A very small quantity of an isomeric pyridone derivative (III) was isolated from the mother-liquor of the reaction mixture.



(I)



(II)



(III)

p-Toluoylacetone gives with ammonia an amine, $CH_3 \cdot C(NH_2) = CH \cdot CO \cdot C_6H_4 \cdot CH_3$, m. p. 93°, which on treatment with cyanoacetamide (see Experimental) gave a well crystalline solid, found to be identical with 3-cyano-4-methyl-6-*p*-tolyl-2-pyridone (II), the main

condensation product derived from the condensation of cyanoacetamide with the β-diketone itself (*cf.* Sen and Basu, *J. Indian Chem. Soc.*, 1930, 7, 437).

Next the *O*-ether (IV) of *p*-toluoylacetone was prepared. This *O*-ether reacted with hydroxylamine (a ketonic reagent) evidently to give rise to 3-*p*-tolyl-5-methyl-*iso*xazole (VI), m.p. 73-74°, (*cf.* Claisen, *Ber.*, 1926, 59, 144) as follows: *

$CH_3{\cdot}C(OEt){=}CH{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3(p)$ (IV)

$CH_3{\cdot}C(OEt){=}CH{\cdot}CO{\cdot}Ph$ (V)

$\xrightarrow{NH_2OH}$

$CH_3{\cdot}C{=}CH{-}C{\cdot}C_6H_4{\cdot}CH_3$ (VI)

(O——N)

$CH_3{\cdot}C{-}CH{=}C\,C_6H_4{\cdot}CH_3$ (VII)

(N——O)

Accordingly cyanoacetamide (also a ketonic reagent) might react to form 3-cyano-4-*p*-tolyl-6-methyl-2-pyridone (III). But on condensing the ether (IV) with cyanoacetamide both in presence of Michael's (sodium ethoxide) as well as Knoevenagel's (diethylamine) reagent, only 3-cyano-4-methyl-6-*p*-tolyl-2-pyridone (II) was isolated in almost quantitative yield, the formation of which may be represented in the following way:—

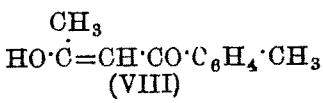
$CH_3{\cdot}C(OEt){:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3 + CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2 \longrightarrow CH_3{\cdot}C(OEt){\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3$ (II)

$CN{\cdot}CH{-}CO{\cdot}NH_2$

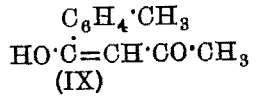
Thus it appears that though the methylene group of cyanoacetamide be regarded as a ketonic reagent, it preferentially reacts with the ethylenic linkage when present in a system as represented in (I) or (IV) (*cf.* Basu, *loc. cit.*). Further the reaction seems to occur mainly through the enol (VIII) which is lightly substituted in the β-position and the yield of the other pyridone derivative (III) is less than 10 per cent. of the total yield, which is even lower than that obtained in the case of benzoylacetone (*cf.* Issoglio, *Atti. R. Accad. Sci. Torino*, 1905, 40, 495). This again exhibits a greater inhibiting effect of a

* The other *iso*xazole derivative 3-methyl-5-*p*-tolyl-*iso*xazole (VII), m. p. 92°, was obtained by the action of hydroxylamine on *p*-toluoylacetone itself.

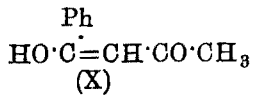
still heavier substituent (tolyl) as present in (IX) in comparison with phenyl in (X).



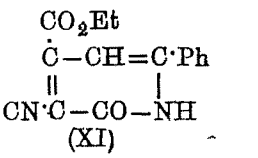
(VIII)



(IX)



(X)

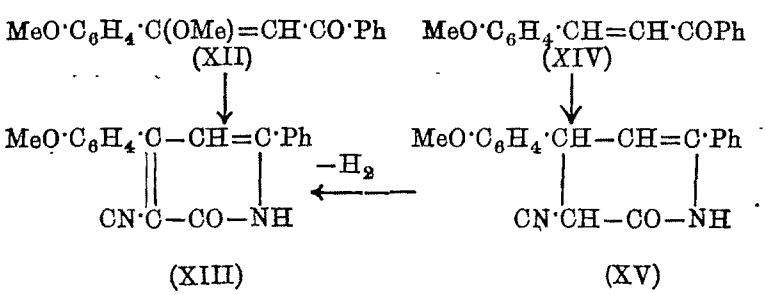


(XI)

By condensing *p*-toluoylacetone with cyanoacetmethylamide the main product was found to be identical with the *N*-methyl ether, 3-cyano-1:4-dimethyl-6-*p*-tolyl-2-pyridone (Formula II, $NH=N\cdot CH_3$) prepared from the pyridone derivative (II).

From the condensation of ethyl benzoylpyruvate with cyanoacetamide a compound, m. p. 229-30°, having the formula $C_{15}H_{12}O_3N_2$ was obtained. This on hydrolysis with fuming hydrochloric acid gave an acid, m. p. 350°, from which the carboxyl group could not be removed even by direct heating. The compound is regarded as ethyl 3-cyano-6-phenyl-2-pyridine-4-carboxylate (XI) (*cf.* Bardhan, *J. Chem. Soc.*, 1929, p. 2223).

Finally another enol ether (XII) has been prepared, and from its condensation with cyanoacetamide 3-cyano-4-anisyl-6-phenyl-2-pyridone (XIII), m. p. 314°, alone was obtained. The constitution of the compound was ascertained by condensing the unsaturated ketone, anisalacetophenone (XIV) with sodiocyanoacetamide when 2-keto-3-cyano-4-anisyl-6-phenyl-1 : 2 : 3 : 4-tetrahydropyridine (XV), m. p. 204-05°, was obtained. This on dehydrogenation with nitrous acid (Barat, *J. Indian Chem. Soc.*, 1930, 7, 330) afforded a product which was found to be identical with (XIII).



(XIII) (XV)

Experimental.

p-Toluoylacetone, $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot CH_3(p)$.—Sodium wire (11·5 g.) was suspended in well-cooled dry ethyl acetate (120 g). The whole being kept in a freezing mixture, dry *p*-methylacetophenone (67 g.) was gradually added with shaking, the addition being completed within 2 to 2½ hours, when the sodium salt began to separate. The mixture was left over for 16 to 18 hours in a cool place. The sodium salt was filtered off, washed with ether and dried over porous plate. It was then dissolved in water and decomposed by dilute acetic acid (30%). The separated oil was taken up in ether and the ethereal solution after being washed with water was dried over anhydrous sodium sulphate. The ether was then driven off and the residual liquid was distilled up to 120°. The remaining oil was distilled under reduced pressure and the fraction boiling between 128° and 140° at 15 mm. was collected. On redistillation at the same pressure it was found to boil at 132° (yield 34 g). (Found: C, 74·92 ; H, 7·03. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·82 per cent.).

It is a colourless, highly refracting liquid, the refractive index being 1·5378 at 28·5°. It gives a reddish-violet coloration with alcoholic ferric chloride.

Copper Salt.—On adding a hot solution of copper acetate to an alcoholic solution of the β-diketone, the copper salt separated, and was crystallised from acetone in small greyish-green needles, m.p. 229°. (Found: Cu, 15·76: $C_{11}H_{11}O_2Cu$ requires Cu, 15·37 per cent.).

Action of Hydroxylamine: Formation of 3-Methyl-5-p-tolyl-isoxazole (VII).—The diketone (2 g.) dissolved in acetic acid was added to an aqueous solution of hydroxylamine hydrochloride (2 g.) and sodium acetate (4 g.), and the mixture was heated on a water-bath for 3 hours when on cooling crystals separated out. These were filtered off and crystallised from dilute methyl alcohol and obtained in large flakes, m.p. 92°. (Found: N, 8·18. $C_{11}H_{11}ON$ requires N, 8·09 per cent.).

Action of Hydrazine: Formation of 3-Methyl-5-p-tolylpyrazole.—*p*-Toluoylacetone (3·3 g.) in acetic acid was similarly treated with an aqueous solution hydrazine sulphate (2·5 g.) and sodium acetate (5 g.). On addition of water to the reaction mixture a crystalline solid separated out. This was collected and crystallised from dilute alcohol when prismatic needles, m.p. 125° were obtained. This was, however, found to melt first at 96° when dipped in a hot bath and

then again at 125°. On just melting the substance in a test tube, moisture condensed on the cooler part indicating the presence of water of crystallisation. The pyrazole derivative was dried over sulphuric acid in *vacuo* when it no longer melted below 125° even if dipped in the hot bath, and on melting the substance no moisture condensed in the cooler part of the test tube. (Found: N, 16·84. $C_{11}H_{12}N_2$ requires N, 16·28 per cent.). It is very soluble in alcohol and benzene, and on recrystallisation from *dilute* alcohol melts at 96° when dipped in hot bath as usual.

Action of Aniline: Formation of $CH_3 \cdot C_6H_4 \cdot CO \cdot CH=CMe \cdot NHPh$.—An acetic acid solution of *p*-toluoylacetone (6 g.) and aniline (3·2 g.) was heated under reflux for about 6 hours, and then cooled in ice when a solid separated out. This was collected and crystallised from methyl alcohol (charcoal) when yellow needles, m.p. 136-37° were obtained. (Found: N, 5·69. $C_{17}H_{17}ON$ requires N, 5·58 per cent.).

Action of Ammonia: Formation of $CH_3 \cdot C_6H_4 \cdot CO \cdot CH=CMe \cdot NH_2$.—Dry ammonia was passed into an alcoholic solution (1:1) of the β-diketone for several hours when on dilution with water the amine separated out. This on crystallisation from a mixture of chloroform and petroleum ether melted at 93°. (Found: N, 8·22. $C_{11}H_{13}ON$ requires N, 8·0 per cent.). It is soluble in most common organic solvents.

An intimate mixture of cyanoacetamide (1 mol.) and the amine (1 mol.) was heated in an oil-bath for more than half an hour at 140° when ammonia was given off and the contents set to a crystalline solid. This on crystallisation from glacial acetic acid formed shining plates, m.p. 330° darkening earlier. (Found: N, 12·58. $C_{14}H_{12}ON_2$ requires N, 12·50 per cent.). It was found to be identical with the main crop obtained from the condensation of *p*-toluoylacetone and cyanoacetamide described below.

Condensation with Cyanoacetamide: Formation of 3-Cyano-4-methyl-6-p-tolyl-2-pyridone (II) *and 3-Cyano-4-p-tolyl-6-methyl-2-pyridone* (III).—Cyanoacetamide (4·2 g.) was dissolved in water by warming and *p*-toluoylacetone (8·8 g.) added with just enough alcohol to effect the solution. Diethylamine (2 c.c.) being added, the solution was warmed up to 60° when after 10 minutes crystals began to separate. After about 2 hours the solid (8·1 g.) was collected and was found to melt at 330°, sintering and darkening a few degrees earlier. The mother-liquor with the further addition of diethylamine

(1 c.c.) was left overnight. Next day the crystals (0·8 g.) were filtered off and dried. This also melted at the same temperature. The operation was repeated when a further crop (0·1 g.) having almost the same melting point was obtained. The mother-liquor was then concentrated to half its volume when a solid (1·0 g.), m.p. 259-61°; was obtained. The filtrate on acidification gave another crop (0·7 g.) melting indifferently between 250° and 270°. The total yield of the condensation product was thus about 10·7 g. (95%).

The first three fractions (9·0 g.) were sparingly soluble in alcohol but crystallised out from glacial acetic acid in shining plates with a faint violet reflex, m p. 330° darkening and sintering earlier. A mixture of this and the product obtained from the amine, $CH_3 \cdot C_6H_4 \cdot CO \cdot CH=CMe \cdot NH_2$ melted at the same temperature. Accordingly this is considered to be 3-cyano-4-methyl-6-*p*-tolyl-2-pyridone (*cf.* Sen and Basu, *loc. cit.*). (Found: N, 12·2. $C_{14}H_{12}ON_2$ requires N, 12·5 per cent.). This pyridone derivative is almost insoluble in common organic solvents but readily dissolves in pyridine and boiling glacial acetic acid. It is also soluble in alkali and concentrated sulphuric acid.

Hydrolysis: *Formation of 4-Methyl-6-p-tolyl-2-pyridone.*—On gently heating the substance with sulphuric acid (80%) for 45 minutes, then pouring the acid solution on ice water and neutralising the solution with solid sodium carbonate, 4-methyl-6-*p*-tolyl-2-pyridone was obtained. This on crystallisation from alcohol diluted with a few drops of water melted at 183°. (Found: N, 7·0. $C_{13}H_{13}ON$ requires N, 7·04 per cent.) It is easily soluble in alcohol, benzene, also soluble in chloroform, carbon tetrachloride and insoluble in ether. It dissolves in caustic soda solution and is obtained unchanged on acidification with dilute hydrochloric acid. The compound in alcoholic solution also imparts a red coloration to ferric chloride.

3-Cyano-1:4-dimethyl-6-p-tolyl-2-pyridone (II, $N \cdot CH_3$ for NH).—To the sodium salt of the pyridone (II) in methyl alcohol, an excess of methyl iodide was added with vigorous shaking. The sodium salt gradually went into solution from which the shining crystals that separated after 12 hours, crystallised from alcohol, m.p. 248°, not depressing when admixed with the *N*-methyl compound described below. (Found: N, 11·95, $C_{15}H_{14}ON_2$ requires N, 11·77 per cent.).

The other isomer *3-cyano-4-p-tolyl-6-methyl-2-pyridone* (III) was isolated from the latter fractions of the condensation product. When

the above two fractions (1·7 g.) were boiled with alcohol (90%), an insoluble portion (about 50%), m.p. 270-300°, was left behind which on crystallisation from glacial acetic acid melted at 330-31° and consequently was 3-cyano-4-methyl-6-*p*-tolyl-2-pyridone. While from the mother-liquor a crystalline solid having no sharp melting point was isolated. This however on repeated crystallisation from dilute alcohol melted indifferently at 275° sintering at 260°. (Found: N, 12·50. $C_{14}H_{12}ON_2$ requires N, 12·50 per cent.). It is also soluble in alkali and sulphuric acid and on hydrolysis with sulphuric acid in the usual way afforded a product which in alcoholic solution gave a brown-red coloration to ferric chloride and on crystallisation from dilute alcohol melted at 253°. Thus it is found that out of the total yield (10·7 g.) of the condensation product the main crop, m.p. 330-31°, constitutes more than 90 per cent.

Condensation of O-Ethyl-p-toluoylacetone (IV) *with Cyanoacetamide: Formation of 3-Cyano-4-methyl-6-p-tolyl-2-pyridone* (II). —The ethyl ether was prepared according to the method described by Claisen (*Ber.*, 1907, **40**, 3909) for the preparation of an analogous ether (V) from benzoylacetone. It was a colourless refracting oil, b.p. 163°/15 mm. *p*-Toluoylacetone (17·6 g.), orthoformic ester (15·5 g.) and alcohol (15 g.) were mixed together and to it anhydrous ferric chloride (0·5 g.) was added. The whole was then boiled for 10 minutes under reflux, rapidly cooled in ice and taken in ether. The ethereal solution was washed first with water and then repeatedly with dilute caustic soda solution (2*N*) until the extract gave no appreciable colour to an alcoholic ferric chloride solution. It was then dried over anhydrous calcium chloride, the ether was distilled off and the residual liquid distilled under reduced pressure when a pale yellow oil (11·5 g.) was collected at 185-87° at 28 mm. pressure. This on redistillation at 15 mm. pressure was obtained as an almost colourless oil, b.p. 163°. (Found: C, 76·08; H, 7·68. $C_{13}H_{16}O_2$ requires C, 76·47; H, 7·84 per cent.). The refractive index is 1·5510 at 35°. It does not give any coloration to ferric chloride solution (neutral) but on the addition of a drop of hydrochloric acid colour at once develops and gradually changes to reddish-violet, the characteristic test of β-diketone itself.

An alcoholic solution of the oil (4·1 g.) was gradually added with shaking to a suspension of sodiocyanoacetamide prepared from cyanoacetamide (1·7 g.) in hot alcohol and sodium (0·46 g.) also dissolved in absolute alcohol. The colour of the mixture at once became

deeper (yellow) and it was left aside with occasional shaking when a granulated sodium salt began to separate within 3 to 4 hours. After 5 days the separated sodium salt was dissolved in water and the solution was acidified with dilute hydrochloric acid when a solid (4·4 g.), m.p. 330°, was isolated (yield 98%). From glacial acetic acid it was obtained in beautiful shining crystals with the characteristic violet reflex of 3-cyano-4-methyl-6-*p*-tolyl-2-pyridone and was found to melt at the same temperature when admixed with the above compound already described. The same pyridone derivative was obtained in almost theoretical yield by condensing the ether with cyanoacetamide in alcoholic solution in presence of diethylamine at the temperature of boiling water-bath.

Action of the Ether on Hydroxylamine: *Formation of* 3-p-*Tolyl*-5-*methylisoxazole* (VI).—An alcoholic solution of *O*-ethyl-*p*-toluoylacetone (2 g.) was added to an aqueous solution of hydroxylamine hydrochloride (2 g.) and caustic soda (2 g.) and the mixture was heated under reflux on a water-bath for more than an hour. The reaction mixture was then cooled in ice and the solid obtained was collected. Crystallising from methyl alcohol with the addition of a few drops of water it was obtained in minute plates, m. p. 73-74°. (Found: N, 8·17. $C_{11}H_{11}ON$ requires N, 8·09 per cent.).

Condensation of p-*Toluoylacetone with Cyanoacetmethylamide*: *Formation of* 3-*Cyano*-1: 4-*dimethyl*-6-p-*tolyl*-2-*pyridone* (II, NH $=NCH_3$) *and* 3-*Cyano*-1: 6-*dimethyl*-4-p-*tolyl*-2-*pyridone* (III, NH $=NCH_3$).—The condensation was effected in the usual way in presence of diethylamine (total yield 91%).

The main product (about 92% of the total yield) crystallises from alcohol (90%) in beautiful shining plates with a violet reflex, m. p. 248°, not depressed on admixture with the *N*-methyl ether previously described and evidently it is 3-*cyano*-1: 4-*dimethyl*-6-p-*tolyl*-2-*pyridone*. (Found: N, 12·05. $C_{15}H_{14}ON_2$ requires N, 11·77 per cent.). This is easily soluble in acetone, chloroform, methyl and ethyl alcohol, moderately so in benzene and carbon tetrachloride, sparingly in boiling water and insoluble in ether. It also dissolves in concentrated sulphuric acid, precipitated unchanged on dilution with water and is insoluble in alkali. On hydrolysis with fuming hydrochloric acid at 150-60° for 4 hours the compound afforded a solid product which on crystallisation from dilute hydrochloric acid was obtained in fine prismatic needles, m.p. 188°. (Found: N, 5·50; Cl, 13·98. $C_{14}H_{15}ON,HCl$ requires N, 5·61; Cl, 14·23 per cent.).

It is a hydrochloride, and when heated to its melting point vapours of hydrogen chloride evolve. The compound gives no coloration to alcoholic ferric chloride.

The product from mother-liquor (0·4 g.), m.p. 158-78°, on twice crystallisation from dilute alcohol melted indifferently at 175-76° sintering earlier. This is regarded as the other isomer *3-cyano-1: 6-dimethyl-4-p-tolyl-2-pyridone*. (Found: N, 11·76. $C_{15}H_{14}ON_2$ requires N, 11·77 per cent.).

Condensation of Ethyl Benzoylpyruvate with Cyanoacetamide: Formation of Ethyl 3-Cyano-6-phenyl-2-pyridone-4-carboxylate (XI).—The condensation was effected as usual by means of diethylamine at the room temperature, the yield being more than 70%. The condensation product crystallised from glacial acetic acid in yellow needles having a green reflex, m. p. 229-30. (Found: N, 10·54. $C_{15}C_{12}O_3N_2$ requires N, 10·45 per cent.). It insoluble in water but soluble in alcohol and acetic acid. It dissolves in alkali with a beautiful violet fluorescence and also in concentrated sulphuric acid. On hydrolysis with fuming hydrochloric acid at 170-75° for more than 4 hours the above pyridone derivative afforded an acid which on crystallisation from a large volume of glacial acetic acid melted at 350°. (Found: N, 6·63. $C_{12}H_9O_3N$ requires N, 6·51 per cent.). It is insoluble in common organic solvents but soluble in pyridine, sodium bicarbonate solution with effervescence and in concentrated sulphuric acid. The acid may also be obtained by simply heating the pyridone derivative with caustic soda solution (10%) for a short time.

Ethyl 1-Methyl-3-cyano-6-phenyl-2-pyridone-4-carboxylate (XI, NH=N·CH_3).—The pyridone derivative dissolved in sodium methoxide solution containing the required quantity of sodium was treated with methyl iodide till the solution was found neutral. Excess of methyl alcohol was distilled off and the oil that was left behind, soon solidified. Water was added and the remaining solid was collected and dried over porous plate. On crystallisation from a mixture of chloroform and petroleum ether it was obtained in rhombic yellow plates, m. p. 150°. (Found: N, 10·26. $C_{16}H_{14}O_3N_2$ requires N, 9·98 per cent.). It is very soluble in almost all organic solvents except petroleum ether in which it is insoluble. It dissolves in concentrated sulphuric acid with a green fluorescence but is insoluble in cold alkali. On boiling however its solution in warm alkali and on acidifying the solution, an acid, m. p. 253°, was obtained.

Condensation of O-Methylanisoylacetophenone, $CH_3O \cdot C_6H_4 \cdot C(OCH_3)=CH.CO \cdot Ph$ (XII) *with Cyanoacetamide*: *Formation of 3-Cyano-4-anisyl-6-phenyl-2-pyridone* (XIII).—The methyl ether was prepared according to Weygand (*Annalen*, 1927, 459, 113) and its condensation with cyanoacetamide effected in the usual way (yield 50%). The product on crystallisation from pyridine was obtained in fine needles, m. p. 314°. (Found: N, 9·02. $C_{19}H_{14}O_2N_2$ requires N, 9·27 per cent.). It is almost insoluble in alcohol, sparingly so in glacial acetic acid but dissolves in alkali and concentrated sulphuric acid. That the compound is 3-cyano-4-anisyl-6-phenyl-2-pyridone is proved from the following investigations.

Condensation of Anisalacetophenone (XIV) *with Cyanoacetamide*: *Formation of 2-Keto-3-cyano-4-anisyl-6-phenyl-1:2:3:4-tetrahydropyridine* (XV).—Anisalacetophenone, was prepared according to Pond and Shoffstali (*J. Amer. Chem. Soc.*, 1900, 22, 666) and Weygand (*loc. cit.*). An alcoholic solution of the unsaturated ketone (1 mol.) was treated with sodiocyanoacetamide (1 mol.) as usual. After 4 days water was added to the reaction mixture and the condensation product was obtained by acidulation with dilute hydrochloric acid. Crystallising from alcohol (90%) it was obtained in clusters of needles, m.p. 204-05°. (Found: C, 75·58; H, 5·57; N, 9·24. $C_{19}H_{16}O_2N_2$ requires C, 75·01; H, 5·26; N, 9·21 per cent.). This compound is also soluble in concentrated sulphuric acid.

Dehydrogenation: *Formation of 3-Cyano-4-anisyl-6-phenyl-2-pyridone* (XIII).—The above pyridine derivative (2 g.) was dissolved in glacial acetic acid and cooled in ice when a similarly well cooled solution of sodium nitrite (1 g.) was slowly added to it. The flask was left for two hours in the ice-bath and then overnight at the room temperature. Next day the solid that separated out was collected and on crystallisation from pyridine (charcoal) was obtained in fine needles, m. p. 314° sintering two or three degrees earlier (Found: N, 8·95. $C_{19}H_{14}O_2N_2$ requires N, 9·27 per cent.). This was found to melt at the same temperature when admixed with the compound obtained from the condensation of *O*-methylanisoylacetophenone (XIII) with cyanoacetamide just described.

The author wishes to express his grateful thanks to Professor H. K. Sen for his keen interest in this investigation and to Messrs I. B. Sen-Gupta and C. Barat for valuable assistance.

Department of Applied Chemistry,
University College of Science
and Technology, Calcutta.

Received December 19, 1930.

Synthesis of Coumarins from Phenols and β-Ketonic Esters using Phosphorus Pentoxide. Part I. Coumarins from Resorcinol and Ethyl Acetoacetates.

By Dukkhaharan Chakravarti.

From a study of the literature on the subject of synthesis of coumarins and chromones from phenols and β-ketonic esters, it appears that Pechmann's method* of the synthesis of coumarins in the presence of sulphuric acid and Simonis' method† of synthesising chromones in presence of phosphorus pentoxide have been accepted as of general application and any contrary view has always met with opposition.

In contradiction to Simonis' observation (Petschek and Simonis, *loc. cit.*) that ethyl acetoacetate did not lead to any definite product, the author, during the course of his attempts to synthesise different hydroxychromones, condensed resorcinol and ethyl acetoacetate in presence of phosphorus pentoxide obtaining a compound (m.p. 185°) identical with β-methylumbelliferone of Pechmann. The complete identity of the two products is established by their mixed melting points, as also by those of their acetyl derivatives. This raises a question about the general applicability of Simonis' method of synthesising chromones; and as such a detailed study of the reaction has been made with regard to various mono-, di- and tri-hydric phenols and β-ketonic esters. The present paper embodies the results of conden-

* Pechmann and Duisberg, *Ber.*, 1883, **16**, 2119; Pechmann and Cohen, *Ber.*, 1884, **17**, 2187; Pechmann, *Ber.*, 1899, **32**, 3681; Pechmann and Hanke, *Ber.*, 1901, **34**, 354; Pechmann and Kraft, *Ber.*, 1901, **34**, 421; Pechmann and Graeger, *Ber.*, 1901, **34**, 378; Biginelli, *Gazzetta*, 1895, **25**, *ii*, 492; Dey, *J. Chem. Soc.*, 1915, **107**, 1606; Held, *Compt. rend.*, 1893, **116**, 720; Fries and Klostermann, *Annalen*, 1908, **362**, 3; Naik, Desai and Desai, *J. Indian Chem. Soc.*, 1929, **6**, 83; Sen and Basu, *ibid*, 1928, **5**, 467; Sen, *ibid*, 1929, **6**, 1925

† Petscheck and Simonis, *Ber.*, 1913, **46**, 2015; Simonis and Lehmann, *Ber.*, 1914, **47**, 697; Simonis and Remmert, *ibid.*, p, 2229; see also Heilbron, Barnes and Morton, *J. Chem. Soc.*, 1923, **123**, 2569.

sations of resorcinol with substituted ethyl acetoacetates in presence of phosphorus pentoxide.

Simonis and Remmert (*Ber.*, 1914, **47**, 2231) condensed resorcinol and ethyl methylacetoacetate in presence of phosphorus pentoxide and isolated a product melting at 262°, which they assumed to be identical with 7-hydroxy-2: 3-dimethylchromone (m.p. 262°) previously obtained and described by Kostanecki and Lloyd (*Ber.*, 1901, **34**, 2948). Simonis maintained the identity of his product with that of Kostanecki without preparing and comparing the derivatives of his own product with those of 7-hydroxy-2: 3-dimethylchromone. That his product is not identical with the chromone follows from the facts given below:—

(*i*) On repeating the experiment a product melting sharply at 256° has now been obtained, the melting point of which never reached 262° as claimed by Simonis and Remmert, even after purification by repeated crystallisations from different solvents.

(*ii*) The melting point of this product (m.p. 256°) was considerably depressed when mixed with a specimen of the chromone prepared synthetically by a slight modification of Kostanecki's method, which consists in heating 2: 4-dihydroxyphenylethylketone with acetic anhydride and fused sodium acetate and subsequent hydrolysis of the acetylchromone.

(*iii*) Moreover it has been noted by Heilbron, Barnes and Morton (*J. Chem. Soc.*, 1923, **123**, 2569) that the compound prepared according to Simonis' method gives different derivatives from those obtained from the chromone of Kostanecki.

(*iv*) Also, the following table,

	I	II	III
	Simonis' compound.	Kostanecki's compound.	Pechmann's compound.
Original compound	m.p. 256° (262° claimed by Simonis).	262°	256°
Acetyl derivative	m.p. 165°	116°	165°
Methyl ether	m.p. 140°	126°	140°
Ethyl ether	m.p. 121°	124°	121°

shows that the compounds of set I are identical with those of set III, proving that the product (m.p. 262°) obtained by Simonis is identical with the one obtained by Pechmann and Duisberg (*loc. cit.*).

Thus the compound of Simonis is a coumarin and not a chromone, the derivatives of which are shown in set II.

Heilbron, Barnes and Morton (*loc. cit.*) having observed that the methyl group in position 2 in 2-methylchromones react with aldehydes in presence of alcoholic sodium ethoxide, attempted to condense the ethyl ether of Simonis' compound with aldehyde; but this being not a true chromone, the attempt failed. They sought to explain away this inactivity of the methyl group as due to the occurrence of the hydroxyl group in position 7. On the other hand 7-methoxy-2: 3-dimethylchromone. prepared now by a modification of Kostanecki's method, is found to react readily, like other 2-methylchromones, with benzaldehyde to form a styrene derivative. Thus the explanation put forward by Heilbron and others falls to the ground inasmuch as the so-called chromone with which they started was really a coumarin.

That 7-methoxy-2-methyl*iso*flavone prepared by Baker and Robinson's method (*J. Chem. Soc.*, 1925, **127**, 1981) has also now been condensed with benzaldehyde in presence of sodium ethoxide to form 7-methoxy-2-styryl-3-phenylchromone melting at 204° and identical with the compound prepared by Baker and Robinson by a different method (*loc. cit.*) is a sufficient proof of the view that the presence of the hydroxyl group in position 7 in a chromone is no hindrance to the reactivity of the 2-methyl-group. It is interesting to note that the isomeric compound obtained by Jacobson and Ghosh (*J. Chem. Soc.*, 1915, **107**, 1053) by the condensation of resorcinol and ethyl phenylacetoacetate does not react with benzaldehyde, thus affording an additional proof of their compound being an α-pyrone and not a γ-pyrone derivative as was claimed by them. The author thinks that the reaction with aldehydes is characteristic of the 2-methylchromones in distinction to the 4-methylcoumarins.

Some other substituted ethyl acetoacetates react with resorcinol exactly like the methyl compound to form coumarins irrespective of the condensing agent used.

In contradiction to the observations of Jacobson and Ghosh (*J. Chem. Soc.*, 1915, **107**, 424) it has been found during the present investigation that a substituent in the ethyl acetoacetate molecule, however heavy or complex, does not in any way favour the formation of a chromone in the case of resorcinol even in the presence of phosphorus pentoxide, the formation of coumarins being instantaneous and complete.

On condensing resorcinol with ethyl benzylacetoacetate under different conditions Jacobson and Ghosh (*J. Chem. Soc.*, 1915, **107**, 426) obtained two compounds melting at 186° and 224°, both yielding the identical acetyl derivative melting at 168°. On repeating the experiment the author obtained only the substance melting at 224° and failed to isolate the one, melting at 186° even after repeated attempts using sulphuric acid, phosphorus pentoxide and sodium ethoxide as condensing agents. Jacobson and Ghosh's explanation that the compound melting at 224° is an additive compound of the one melting at 186° with resorcinol has been now shown to be incorrect in view of the fact that the acetyl derivatives from both the compounds produce, on deacetylation, the compound melting at 224° and not the one melting at 186°. Hence it seems that their compound with m.p. 186° was an impure product and the one melting at 224° was 7-hydroxy-3-benzyl-4-methylcoumarin.

Resorcinol has also been condensed with acetonedicarboxylic acid in presence of phosphorus pentoxide to form 7-hydroxycoumarin-4-acetic acid, previously prepared by Burton and Pechmann (*Annalen*, 1897, **261**, 167). Incidentally it may be noted that coumarins are readily formed in the presence of sodium ethoxide as the condensing agent. Several cases have been studied with ethyl acetoacetate and its *C*-methyl and *C*-benzyl derivatives.

EXPERIMENTAL.

αβ-Dimethylumbelliferone (*7-Hydroxy-3:4-dimethylcoumarin*) was prepared according to Pechmann's method (Pechmann and Duisberg, *loc. cit.*) formed colourless needles, m.p 256°.

The *acetyl* derivative, prepared in the usual manner, crystallises from alcohol in colourless needles, m.p. 165°. (Found: C, 67·32; H, 5·30. $C_{13}H_{12}O_4$ requires C, 67·24; H, 5·17 per cent.).

The *methyl ether*, prepared by means of dimethyl sulphate crystallises from alcohol in colourless needles, m.p. 140°. (Found: C, 70·55; H, 6·10. $C_{12}H_{12}O_3$ requires C, 70·59; H, 5·88 per cent.).

The *ethyl ether*, prepared by the action of ethyl iodide in presence of sodium ethoxide in alcoholic solution crystallises in colourless prisms from alcohol, m.p. 121°. (Found: C, 71·39; H, 6·51. $C_{13}H_{14}O_3$ requires C, 71·56; H, 6·42 per cent.).

The same αβ-dimethylumbelliferone is obtained by the interaction of resorcinol (10 g.), ethyl methylacetoacetate (10 g.) and

phosphorus pentoxide (85 g.). Vigorous reaction sets in in the cold with much evolution of heat. The flask is finally heated for half an hour on a boiling water-bath. The cold mass is treated with water and the brown solid is washed with water and crystallised from alcohol (charcoal) as colourless needles, m.p. 256°, the melting point being not depressed when mixed with a sample of $\alpha\beta$-dimethylumbelliferone prepared by using sulphuric acid.

The identical compound is also obtained with sodium ethoxide as the condensing agent. Resorcinol (4 g.) is added to a solution of ethyl methylacetoacetate (4 g.) in an alcoholic solution of sodium ethoxide (1 g. sodium in 25 c.c. alcohol) and the solution heated for 15 minutes on the water-bath, when the sodium salt of the coumarin separates in quantity. The solution is then poured into an excess of water, acidified with dilute hydrochloric acid and the precipitate crystallised from dilute alcohol, m.p. 256° (acetyl derivative, m.p. 165°, methyl ether, m.p. 140°, ethyl ether, m.p. 121°).

Preparation of 2:4-Dihydroxyphenylethylketone.—It is prepared by heating resorcinol (20 g.), propionic acid (17 g.) and zinc chloride (40 g.) for three hours at 140-60°. The red liquid is poured into ice and the pasty solid that separates out is repeatedly extracted with cold benzene, when long yellow needles separate as the benzene evaporates away. When crystallised from dilute alcohol, it is obtained as a colourless substance, m.p. 100° (yield 8 g.). Goldsweig and Kaiser (*J. Chem. Soc.*, 1891, **60**, 447) records it to be a ruddy-yellow substance, m.p. 97°.

The *acetyl* derivative of the above is prepared by heating at 180° a mixture of the ketone (10 g.), acetic anhydride (40 c.c.) and anhydrous sodium acetate (10 g.) under reflux for 12 hours. The product is poured into water, slightly warmed and crystallised from dilute alcohol m.p. 116°. The acetyl derivative, on hydrolysis with sodium carbonate, gives the hydroxychromone (m.p. 262°) which on treatment with dimethyl sulphate produces 7-methoxy-2:8-dimethylchromone (m.p. 126°) (*cf.* Kostanecki and Lloyd, *loc. cit.*).

Interaction of 7-Methoxy-2.3-dimethylchromone and Benzaldehyde: Formation of 7-Methoxy-2-styryl-3-methylchromone.—The chromone (1 g.) is dissolved in the least quantity of absolute alcohol and an alcoholic solution of sodium ethoxide and benzaldehyde (1 g.) are added to it. The solution is kept overnight, when on slight warming on the water-bath, crystals separate. These are filtered off, washed with rectified spirit and finally recrystallised from alcohol,

m.p. 152° (yield quantitative). (Found: C, 78·02; H, 5·55. $C_{19}H_{16}O_3$ requires C, 78·08 ; H, 5·48 per cent.).

Interaction of 7-Methoxy-2-methylisoflavone and Benzaldehyde: Formation of 7-Methoxy-2-styrylisoflavone.—The 7-methoxy-2-methyl-*iso*flavone is dissolved in the minimum quantity of absolute alcohol and an alcoholic solution of sodium ethoxide and benzaldehyde (1 g.) is added to it. Crystals separate out on keeping the solution overnight. The crystals are filtered, washed with alcohol and finally recrystallised from glacial acetic acid containing a few drops of water. Colourless needles, sparingly soluble in alcohol, m.p. 204°, (yield quantitative) identical with the compound prepared by Baker and Robinson (*loc. cit.*) by a different method. (Found: C, 81·2 ; H, 5·21. $C_{24}H_{18}O_3$ requires C, 81·35 ; H, 5·08 per cent.).

7-Hydroxy-3-benzyl-4-methylcoumarin.—Phosphorus pentoxide (35 g.) is added to a mixture of resorcinol (6 g.) and ethyl benzylacetoacetate (10 g.). The mixture is heated for five minutes on the water-bath, when a vigorous reaction sets in. The flask is then immediately cooled under water and treated with water, when a viscous oil separates. The oil is separated, dissolved in dilute caustic soda solution, extracted with ether and the clear aqueous solution acidified. The heavy oil, thus obtained, is again dissolved in dilute alkali and precipitated with carbon dioxide. The brown solid is crystallised from alcohol (charcoal) as colourless prisms, m.p. 224°. (Found after drying at 120-30°: C, 76·27; H, 5·33. $C_{17}H_{14}O_3$ requires C, 76·69 ; H, 5·26 per cent.).

The *acetyl* derivative crystallises from dilute alcohol in colourless needles, m.p. 168°, being identical with the acetyl derivative of the product melting at 186°, isolated by Jacobson and Ghosh (*loc. cit*).

The *methyl ether* crystallises from alcohol in colourless needles, m.p. 119°, and is identical with the methyl ether of the product melting at 186° isolated by Jacobson and Ghosh. (Found: C, 77·01; H, 5·82. $C_{18}H_{16}O_3$ requires C, 77·14 ; H, 5·71 per cent.).

The *acetyl* derivative, on deacetylation by boiling for an hour with 40% sulphuric acid, yields the original product melting at 224°. (Found: C, 76·21; H, 5·45. $C_{17}H_{14}O_3$ requires C, 76·69; H, 5·26 per cent.).

The condensation of resorcinol (3 g.), ethyl benzylacetoacetate (5 g.) in presence of sulphuric acid (20 c.c.) according to Jacobson and Ghosh's method also yields the identical coumarin, m.p. 224°. The product obtained by the condensation in presence of

sodium ethoxide (1 g. sodium in 35 c.c. alcohol) of resorcinol (2 g.) and ethyl benzylacetoacetate (5 g.) also melts at 224°.

7-Hydroxy-8-ethyl-4-methylcoumarin was prepared from resorcinol and ethyl ethylacetoacetate in presence of concentrated sulphuric acid or phosphorus pentoxide. It crystallises from dilute alcohol in colourless needles, m.p. 194-98°. (Found: C, 70·50 ; H, 5·92. $C_{12}H_{12}O_3$ requires C, 70·59 ; H, 5·88 per cent.).

The *acetyl* derivative crystallises from dilute alcohol in colourless prisms, m.p. 110°. (Found: C, 68·22; H, 5·75. $C_{14}H_{14}O_4$ requires C, 68·29; H, 5·69 per cent.).

The *methyl ether* crystallises from dilute alcohol in colourless needles, m.p. 98°. (Found: C, 71·51 ; H, 6·49. $C_{13}H_{14}O_3$ requires C, 71·56 ; H, 6·42 per cent.).

7-Hydroxy-8-propyl-4-methylcoumarin was prepared from resorcinol and ethyl propylacetoacetate in presence of concentrated sulphuric acid or phosphorus pentoxide. In the latter case the mixture is heated for half an hour on the water-bath with a few drops of absolute alcohol ; the pasty solid obtained on adding water is dissolved in dilute alkali, the alkaline solution extracted with ether and the aqueous solution acidified. It crystallises in colourless prisms from dilute alcohol, m.p. 169-71°. (Found: C, 71·32 ; H, 6·30. $C_{13}H_{14}O_3$ requires C, 71·56 ; H, 6·42 per cent.).

The *acetyl* derivative, crystallises in rectangular plates from dilute alcohol, m.p. 119°. (Found: C, 69·12 ; H, 6·19. $C_{15}H_{16}O_4$ requires C, 69·23 ; H, 6·15 per cent.).

*7-Hydroxy-8-iso*propyl-4-*methylcoumarin* was prepared from resorcinol and ethyl *iso*propylacetoacetate in presence of concentrated sulphuric acid or phosphorus pentoxide as in the above case. It crystallises from dilute alcohol in colourless needles, m.p. 224°. (Found: C, 71·58; H, 6·46. $C_{13}H_{14}O_3$ requires C, 71·56; H, 6·42 per cent.).

The *acetyl* derivative crystallises from alcohol in colourless plates, m.p. 124°. (Found: C, 69·32; H, 6·21. $C_{15}H_{16}O_4$ requires C, 69·23 ; H, 6·15 per cent.).

*7-Hydroxy-8-iso*butyl-4-*methylcoumarin* was prepared from resorcinol and ethyl *iso*butylacetoacetate in presence of concentrated sulphuric acid or phosphorus pentoxide. In the latter case the oil, separating on adding water is extracted with ether, the ethereal solution washed with dilute caustic soda and the aqueous alkaline solution precipitated with carbon dioxide. It crystallises from dilute

alcohol in colourless plates, m.p. 153°. (Found: C, 72·22 ; H, 7·1. $C_{14}H_{16}O_3$ requires C, 72·41 ; H, 6·90 per cent.).

The *acetyl* derivative crystallises from dilute alcohol in colourless plates, m.p. 109°. (Found: C, 69·91; H, 6·63. $C_{16}H_{18}O_4$ requires C, 70·07 ; H, 6·57 per cent.).

7-Hydroxy-3-phenyl-4-methylcoumarin was prepared by adding phosphorus pentoxide in the cold to a solution of resorcinol and ethyl phenylacetoacetate in a few c.c. of absolute alcohol. The reaction is almost complete in the cold. It melts at 226° and its acetyl derivative melts at 185°, hence it is identical with the compound prepared with sulphuric acid by Jacobson and Ghosh (*loc. cit.*).

The *methyl ether*, prepared with the help of dimethyl sulphate and caustic soda, melts at 104° and not at 87° as recorded by Jacobson and Ghosh. (Found: C, 76·23; H, 5·42. $C_{17}H_{14}O_3$ requires C, 76·69 ; H, 5·26 per cent.).

7-Hydroxy-3-chloro-4-methylcoumarin (m.p. 236°, acetyl derivative, m.p. 161°), identical with Pechmann and Hanke's compound (*Ber.*, 1901, **34**, 354) is obtained by adding phosphorus pentoxide to a solution of resorcinol and ethyl chloroacetoacetate in a few c.c. of alcohol.

My grateful thanks are due to Prof. R. N. Sen for his valuable suggestions and kind interest throughout the progress of the work.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Received February 9, 1931.

Condensation of Acetonedicarboxylic Acid with Phenols and Phenolic Ethers. Part I. Formation of β-Substituted Glutaconic Acids.

By Dattatraya Balkrishna Limaye and Vishnu Mahadeva Bhave.

Condensation of phenols with β-ketonic acids or esters takes place in the *ortho*-position to the hydroxyl group resulting in the formation of coumarins and chromones.*

During the synthesis of coumaryl-4-acetic acid from phenol, (Limaye, *J. Indian Chem. Soc.*, 1927, **4**, 159) the formation of a dicarboxylic acid as a by-product was observed which was thought to belong to the *para*-series. This observation has since been confirmed, a modified process giving better yield worked out and the reaction extended to phenolic ethers, anisole and *o*-cresol methyl ether, by Limaye and Dixit (*Proc. Indian Science Congress*, 1930, p. 167). That the condensation takes place in the *para*-position with respect to the hydroxyl group is proved by the fact that the products on oxidation give known *para*-substituted acids. Thus phenol, when condensed with acetonedicarboxylic acid in the presence of sulphuric acid gives a dicarboxylic acid, $C_{11}H_{10}O_5$, the methyl ether of which is identical with the product directly obtained from anisole and gives anisic acid on oxidation.

As previous workers had not observed the formation of *para*-substituted products in this type of condensation, stress was laid at first on this aspect of the reaction. But the isolation of the dicarboxylic acids opens out a new field of investigation, since these acids can be looked upon as β-substituted glutaconic acids.

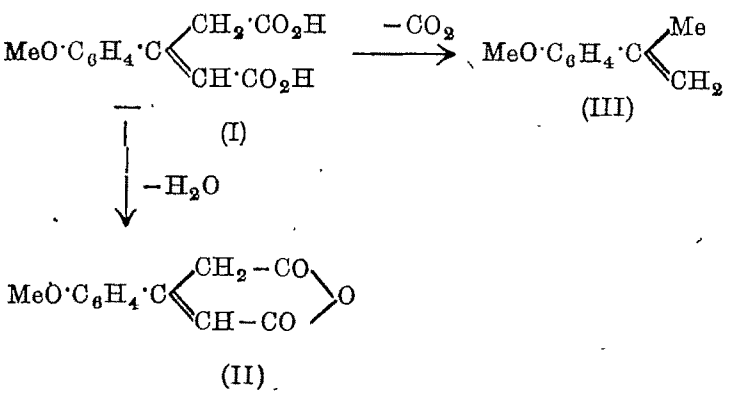
Dey (*J. Chem. Soc.*, 1915, **107**, 1606) had tried to obtain glutaconic acids of the *ortho*-series by the hydrolysis of the corresponding coumarinacetic acids but he was not able to isolate such acids in the free state except in the case of the product from β-naphthol, since these acids reverted to the coumarin structure by the

* For a list of references *vide* Sen and Basu, *J. Indian Chem. Soc.*, 1928, **5**, 467; also Naik, Desai and Trivedi, *J. Indian Chem. Soc.*, 1929, **6**, 801.

loss of water. But as the process now developed gives acids substituted in the *para*-position, the conversion to coumarinacetic acids is obviated.

The great interest attaching to the constitution of glutaconic acids in general and the ready availability of these acids by the new method, as compared to the difficulties mentioned by Bland and Thorpe (*J. Chem. Soc.*, 1912, **101**, 856) have led us to undertake their further investigation.

In the present paper evidence has been recorded to show that the dibasic acid from anisole, which might be taken as typical of this series of acids, has really the constitution of a β-substituted glutaconic acid. Thus the acid from anisole (I) gives, by loss of carbon dioxide, the known *p*-methoxy*iso*propylenebenzene (III) (Behal and Tiffeneau, *Compt. rend.*, 1901, **132**, 561). It also gives an anhydride (II) and resembles the well-known β-phenylglutaconic acid in properties.



Moreover, semicarbazide hydrochloride has been found to react with the anhydrides of β-substituted glutaconic acids for the first time. However as there are difficulties in ascribing a semicarbazone structure to these derivatives, which seem to be additive products, work is in progress to elucidate their real constitution. The action of acetic anhydride on these glutaconic acids is also being studied in detail. The results so far obtained, which lead us to reconsider the structure of an hydroxy anhydride assigned by Thorpe and his co-workers to the anhydrides of β-substituted glutaconic acids, to account for their ready titratibility with alkalis, apparently as monobasic acids, and their reaction with ferric chloride, will be communicated in due course.

Experimental.

β-4-Methoxyphenylglutaconic Acid.—To the acetonedicarboxylic acid mixture prepared from 25 g. of citric acid and 40 c.c. of pure concentrated sulphuric acid, after the method of Dey and Row (*J. Indian Chem. Soc.*, 1924, 1, 112), 10 c.c. of anisole are added. The flask is allowed to stand at the room temperature (25°) for two hours, after which the contents are poured in about 150 c.c. of water. The crystalline precipitate which separates is washed with cold water and crystallized from boiling water. It is then further purified by conversion into the barium salt and its subsequent decomposition with dilute hydrochloric acid. The acid thus obtained (about 2 g.) melts at 176° (decomp.) and is insoluble in benzene. (Found: C, 61·1 ; H, 5·1 ; equi. wt., 118. $C_{12}H_{12}O_5$ requires C, 61·0 ; H, 5·1 per cent., equi. wt., 118).

Anhydride of β-4-Methoxyphenylglutaconic Acid.

(*a*) *By heating.*—The acid (I) is heated in an oil-bath at 180° for half an hour. The product is crystallized from benzene; m.p. 160°. It titrates as a monobasic acid with alkali and in alcoholic solution, gives with ferric chloride, a greenish-blue coloration which disappears on keeping. (Found: C, 66·0; H, 4·5; equi. wt., 217. $C_{12}H_{10}O_4$ requires C, 66·1; H, 4·6 per cent., equi. wt., 218).

(*b*) *By acetic anhydride.*—The acid (I) (5 g.) is boiled with acetic anhydride (10 c.c.) for five minutes and the solution is allowed to cool. The crystals which separate are filtered, washed with dry ether and recrystallised from benzene, m. p. 160° and are identical with the above compound.

p-*Methoxy*iso*propylenebenzene* (II).

(*a*) *By dry distillation with lime.*—The dibasic acid (I) is heated with lime in a flask with a side tube. A small quantity of liquid distils over which, after steam distillation, gives a white solid melting at 32·5° (yield 10-15%.) (Found: C, 81·2 ; H, 8·0. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1 per cent.).

(*b*) *By boiling with mineral acid.*—The acid (I) (5 g.) is boiled with 30 c.c. of 10% hydrochloric acid for 15 minutes and then subjected to steam distillation when a solid melting at 33° passes over.

The decarboxylated product obtained in both the above processes was identical with *p*-methoxy*iso*propylenebenzene (Behal and

Tiffeneau, *loc. cit.*) which was prepared from ethyl anisate and methyl magnesium iodide (Klages, *Ber.*, 1904, **37**, 3995). The same compound was also prepared for identification by heating β-methyl-*p*-methoxycinnamic acid with lime.

The Acid-Ester of the Dibasic Acid, (I).—The anhydride (III) (1 g.) and 5 c.c. of absolute alcohol are boiled for five hours under reflux. The excess of alcohol is driven off on a water-bath. The residue is dissolved in ether and the ethereal solution is extracted with sodium carbonate solution. On acidifying the alkaline extract a white product separates which on crystallisation from water melts at 126-27°. (Found: equi. wt., 263. $C_{14}H_{16}O_5$ requires equi. wt., 264).

Semianilide of β-4-Methoxyphenylglutaconic Acid.

(*a*) *From the anhydride.*—The anhydride (III) (1 g.) is dissolved in 40 c.c. of warm benzene and 0·5 g. of aniline added. After a few seconds a precipitate begins to separate and increases in volume on keeping. The reaction is completed by warming on the water-bath. On cooling the precipitate is filtered and exactly neutralized with alkali. The clear solution is warmed and a slight excess of barium chloride solution is added. The small quantity of precipitate which separates is filtered off and the filtrate acidified with dilute hydrochloric acid. The semianilide separates as a white precipitate (1 g.) and is crystallised from alcohol, m. p. 89-190° (decomp.). (Found: C, 69·2; H, 5·6 ; equi. wt., 309. $C_{18}H_{17}O_4N$ requires C, 69·4 ; H, 5·5 per cent., equi. wt., 311).

(*b*) *From the dibasic acid*, (I).—The acid (10 g.) is heated with aniline (4·5 g.) on a water-bath for two hours. The resulting mass is washed with dilute hydrochloric acid and the residue purified as in (*a*); m. p. 190° (decomp.). The semianilide is readily convertible into the anil by heating.

Anil of β-4-Methoxyphenylglutaconic acid.

It can be prepared—

(*a*) By boiling 1 g. of the acid with 2 c.c. of aniline for 10 minutes.

(*b*) By heating 1 g. of the acid with 1·25 g. anlline in an oil-bath at 140° for five hours (yield 0·8 g.).

(*c*) By heating the semianilide of the acid at 200° for one hour.

The resinous mass obtained in each case is washed with dilute hydrochloric acid or ether and then rapidly recrystallised first from

alcohol or glacial acetic acid and then from benzene ; m. p. 204-5° (Found : C, 73·6 ; H, 5·0; equi. wt., 292·5. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·1, equi. wt., 293 per cent.).

Action of Semicarbazide Hydrochloride on the Anhydrides of β-Substituted Glutaconic Acids.

(*a*) β-4-Methoxyphenylglutaconic acid anhydride (0·5 g.) is dissolved in 30 c.c. of alcohol and 5 c.c. of 10% semicarbazide hydrochloride solution added. The mixture is well shaken and allowed to stand for a few hours. The white crystalline precipitate which separates is collected and recrystallised from alcohol ; m. p. 208·9° (decomp.).

(*b*) β-Phenylglutaconic anhydride (0·5 g.) gives under identical conditions a crystalline compound, m.p. 193°.

Both these products are readily titratable with alkali and the equivalents found indicate an addition of a semicarbazide molecule to the anhydride.

THE RANADE INDUSTRIAL AND ECONOMIC INSTITUTE,
POONA, 4.

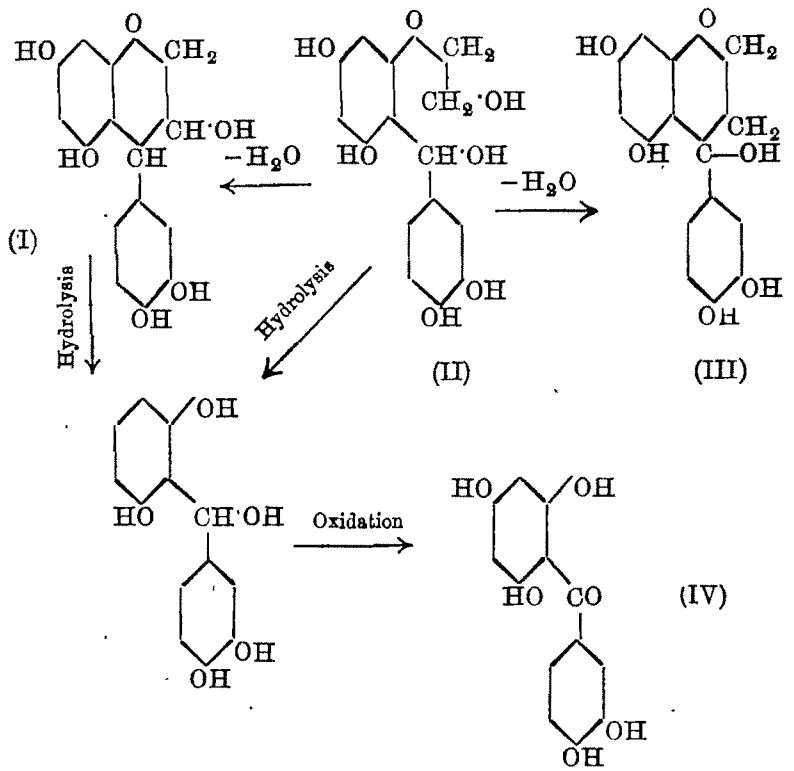
Received March 31, 1930.

On the Presence of Maclurin in the Sapwood of the Cutch-producing Acacias.

By M. Nierenstein.

The yellow colour of the sapwood, if compared with the red-brown colour of the heart-wood, is very striking in the cutch-producing acacias, and since quercetin has been shown to be present in cutch (Löwe, *Z. anal. Chem.*, 1874, **13**, 113; Hlasiwetz, *Annalen*, 1877, **186**, 327; Gauthier, *Bull. Soc. chim.*, 1873, **30**, 567; Perkin and Yoshitake, *J. Chem. Soc.*, 1902, **81**, 1167), it seemed likely that the sapwood may contain quercetin. It has now been shown that this is not the case, as the sapwood of *Acacia catechu*, *A. Catechuoides* and *A. Sundra* has been found to contain maclurin only. The absence of quercetin in the cutch-producing plants thus confirms the contention (Nierenstein, *Ber.*, 1923, **56**, 1877) that quercetin, if present in cutch, is of foreign origin. All attempts to co-ordinate the chemistry of catechin with that of quercetin (Hlasiwetz, *loc. cit.*; Perkin and Yoshitake, *loc. cit.*; Ryan and Walsh, *Proc. Roy. Soc. Dublin*, 1906, **15**, 113) are thus obviously unjustifiable. On the other hand, the presence of maclurin (IV) in the sapwood provides interesting evidence as to the place of catechin in the metabolism of these acacias. It has already been pointed out (Nierenstein, *J. Amer. Chem. Soc.*, 1930, **52**, 1872) that since catechin is only found in the heart-wood, it must be a final product of metabolism. This was confirmed by the discovery of *l*-leucomaclurin-glycol ether (II) in the young twigs of *Acacia Catechu*. It will be realised that the production of acacatechin (I) and *iso*acacatechin (III) from *l*-leucomaclurin-glycol ether (II) follows as a matter of fact, and this was confirmed experimentally in the case of acacatechin, when it was shown that *l*-leucomaclurin-glycol ether on boiling with acetic anhydride yields penta-acetyl-*l*-acacatechin (Nierenstein, *J. Amer. Chem. Soc.*, 1930, **52**, 1676). This obviously goes to show that *l*-leucomaclurin-glycol ether (II), which is present in the young twigs,

is the first product of metabolism, from which (*i*) maclurin (IV) is produced in the sapwood on hydrolysis and oxidation, in the same manner as it is formed when acacatechin (I) is reacted on by *Penicillium solitam* (Hazleton and Nierenstein, *J. Amer. Chem. Soc.*, 1924, **46**, 2100) and (*ii*) the two water-insoluble catechins, (I) and (III), are deposited in the heart-wood by the intramolecular loss of water.



EXPERIMENTAL.

The sapwood of the three acacias investigated separately was obtained by turning the logs freed from the bark in a lathe. It was exhaustively extracted with ethyl acetate in a large Soxhlet apparatus. The residue left on evaporation of the ethyl acetate was dissolved in water, and the aqueous solution shaken with fat-free caseinogen to remove tannins (*cf.* Körner and Nierenstein, *Chem. Z.*, 1911, **36**, 81; Nierenstein, *J. Chem. Soc.*, 1919, **115**, 1330). The filtered solution gave on concentration *in vacuo* crude maclurin (average yield 0·4 g. from 1 kg. sapwood), which on several recrystallisations from

water melted in the anhydrous state (dried at 100° in a vacuum over phosphorus pentoxide) at 220-22°, but became resinous at about 208-10°. On methylation with diazomethane in the manner already described (Hazleton and Nierenstein, *loc. cit.*, p. 2104) the well-crystallising pentamethyl-derivative melting correctly at 157° was obtained. (Found: C, 65·23; H, 6·21. $C_{18}H_{20}O_6$ requires C, 65·17; H, 5·98 per cent.). The pentamethyl ether was found to be in every respect identical with authentic pentamethylmaclurin (mixed m. p. 157°).

THE UNIVERSITY,
BRISTOL, ENGLAND.

Received December 15, 1930.

The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds of the Thiazole Type in Relation to Modern Electronic Conceptions.

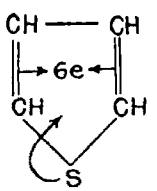
By George Malcolm Dyson, Robert Fergus Hunter, John William Thomas Jones, and Eric Rofe Styles.

The objects of publishing this paper are twofold. Firstly, it has more than once been suggested to one of us that it would be of considerable advantage to summarise the views which we have expressed at different times during the last six years with regard to the unsaturation and tautomeric mobility of heterocyclic compounds of the thiazole type. Secondly, we wish to take this opportunity to place on record a large variety of experimental data which has been accumulated during these years. As is natural with research work of this kind, it has become necessary to seriously revise many of the speculations which were made in the earlier publications.*

In the first place, the whole gist of the work which has been carried out by us in the last few years has been to emphasise the fact that the relation which thiophen bears to benzene is similarly borne by thiazole to pyridine, and by benzthiazole to quinoline. In the thiazole nucleus, the dominating factor in unsaturation and therefore in chemical reactivity, is the nuclear *nitrogen* atom. The explanation which may be given of this in terms of current electronic theories is shown by the formulæ (I), (II) and (III), in which "aromatic character" is attributed to the formation

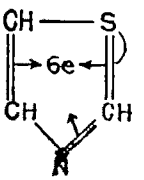
* The papers are denoted in the text by the following numbers: (1) Hunter, *J. Chem. Soc.*, 1925, 127, 1318; (2) Hunter, *J. Chem. Soc.*, 1925, 127, 1488; (3) Hunter, *J. Chem. Soc.*, 1925, 127, 2023; (4) Hunter, *ibid.*, p. 2270; (5) Hunter, *J. Chem. Soc.*, 1926, p. 533; (6) Hunter, *ibid.*, p. 537; (7) Hunter, *J. Chem. Soc.*, 1926, p. 1385; (8) Hunter, *ibid.*, p. 1401; (9) Hunter, *J. Chem. Soc.*, 1926, p. 2951; (10) Hunter and Soyka, *ibid*, p. 2958; (11) Dyson, Hunter and Soyka, *J. Chem. Soc.*, 1926, p. 2964; (12) Dyson, Hunter and Morris, *J. Chem. Soc.*, 1927, p. 1186; (13) Hunter and Styles, *ibid*, p. 1209; (14) Hunter and Styles, *J. Chem. Soc.*, 1928, p. 3019; (15) Dyson, Hunter and Soyka, *J. Chem. Soc.*, 1929, p. 458; (16) Hunter and Pride, *ibid.*, p. 943; (17) Hunter, *J. Chem. Soc.*, 1930, p. 125; (18) Hunter and Jones, *ibid.*, p. 941; (19) Hunter and Jones, *J. Chem. Soc.*, 1930, p. 2190.

of a sextuple group (compare Armit and Robinson, *J. Chem. Soc.*, 1925, **127**, 1605; Goss and Ingold, *J. Chem. Soc.*, 1928, p. 1268) on the lines foreshadowed by Bamberger (*Ber.*, 1891, **24**, 1758; 1893, **26**, 1946; *Annalen*, 1893, **273**, 373), and in which each arrow represents a contributing duplet (compare also Ingold, *Annual Reports of the Chemical Society*, 1928, p. 120). Thus, in thiophen the formation of the sextuple group necessitates calling on a lone pair of electrons of the sulphur atom which results in the inertness of this towards bromine, alkyl halides, and similar reagents. In pyridine (II), on the other hand, the sextuple group is completed without calling on the lone pair of electrons of the nitrogen atom which are therefore available for salt formation. Thiazole is therefore to be represented by a formula (III), and it is noteworthy that it is the nuclear sulp hur atom which contributes the electrons necessary to the formation of the sextuple group.



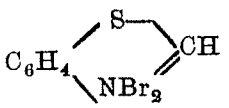
(I)

(II)

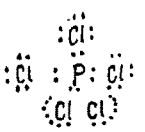


(III)

It has been shown (17) that the bromination of benzthiazole itself yields a dibromide (IV) in which the labile bromine atoms are considered to be held to the nuclear nitrogen atom by means of semipolar single bonds, after the manner in which Prideaux (*Chem. and Ind.*, 1923, **42**, 672) supposes the labile chlorine atoms to be held to the phosphorus atom in phosphorus pentachloride (V) (compare Ingold and Ingold, *J. Chem. Soc.*, 1926, p. 1315; Sugden, *J. Chem. Soc.*, 1927, p. 1173).



(IV)



(V)

On such a basis, benzthiazole dibromide and the dibromides of the 5-chloro-8-bromo-1-alkylaminobenzthiazoles described in this paper therefore become mere analogues of the pentahalides of phosphorus

and antimony, but possess considerable interest in providing examples of the manifestation of valency relationships of this type, occuring in an element of atomic number lower than that of neon. This formulation also enables the octet rule to be maintained, but necessitates abandoning the duplet rule of Lewis.

A singlet linkage must consist of half a covalency and half an electrovalency (Ingold and Ingold, *loc. cit.*). If, therefore, a shared electron is counted as half value for each of the atoms which share it (Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285), there should be a positive charge on the nuclear nitrogen atom in the benzthiazole dibromides and an effective half negative charge on each of the labile bromine atoms which are held by singlets. As Sugden has already pointed out (*loc. cit.*), such half charges can be interpreted dynamically on the lines suggested by Hojendahl (*J. Chem. Soc.*, 1924, **125**, 1381) as a statistical average obtained by intergrating the field of the electron in the neighbourhood of a particular atom over a time interval which is large compared with the period of revolution of its orbit.

It may be noted that a formula similar to (IV) was suggested by Thomson (*Phil. Mag.*, 1921, **41**, 516) for the hypothetical NCl_5, and although this compound is evidently incapable of existence, the formation of bromo-addition compounds by pyridines (Trowbridge, *J. Amer. Chem. Soc.*, 1897, **19**, 558) and benzthiazoles suggests the possibility of the existence of a pentafluoride of nitrogen.

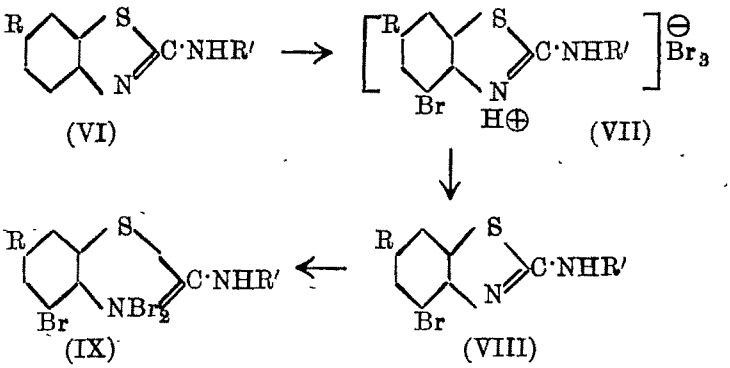
Unfortunate difficulties which present themselves in the study of benzthiazole dibromide are, however, the extreme sensitivity of the compound to the atmosphere, and the ease with which it undergoes nuclear substitution in contact with hydroxylic solvents. For the purpose of strengthening the evidence in favour of our view with regard to the constitution of such compounds, it was therefore desirable to prepare stable compounds of this class for the purpose of more detailed examination.

At the same time it was considered of interest to examine more closely the increase in unsaturation accompanying an increase in the atomic volume of the alkyl group in a homologous series of 1-alkylaminobenzthiazoles (VI), and attempts were therefore directed towards the preparation of a series of stable 1-alkylaminobenzthiazole dibromides.

The bromination of a series of 1-*alkylamino*-5-*methylbenzthiazoles* (VI, R=Me); synthesised from the corresponding sym-p-*tolylalkyl*-

thiocarbamides by treatment with bromine under the usual conditions (3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16), was first studied.

The consumate ease with which bromine enters the *ortho*-position to the nuclear nitrogen atom in such bases, however, resulted in the production of *hydrotribromides* of the corresponding 3-bromo-1-alkylamino-5-methylbenzthiazoles (VII, R=Me, R'=Me, Et, *n*-Pr, and *iso*-C_4H_9).



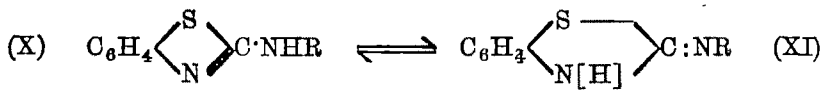
The bromination of the *3-bromo-1-alkylamino-5-methylbenzthiazoles* (VIII, R=Me) obtained by reduction of the hydrotribromides by sulphurous acid, unfortunately gave rise to gummy bromo-addition products which could not be investigated.

Attention was therefore directed to the *5-chloro-1-alkylaminobenzthiazoles* (VI, R=Cl) in which it appeared probable that the presence of the *para*-halogen atom would suppress the tendency towards nuclear substitution by bromine (compare Fries, *Annalen*, 1906, **346**, 128). Actually, however, the 5-chloro-bases behaved perfectly analogously to the 1-alkylamino-5-methylbenzthiazoles, and gave rise to *hydrotribromides* of the 5-chloro-3-bromo-1-alkylaminobenzthiazoles on bromination in chloroform.

The bromination of the 5-chloro-3-bromo-*bases* (VIII, R=Cl) yielded a series of stable *dibromides* (IX, R=Cl) of the required type, and a careful study was made of certain of these compounds.

In 1926, it was suggested (9, 10) that on the basis of the modified strain theory of Ingold (*J. Chem. Soc.*, 1921, **119**, 305, 951; compare also Deshapande and Thorpe, *J. Chem. Soc.*, 1922, **121**, 1432; Bains and Thorpe, *J. Chem. Soc.*, 1923, **123**, 1206; Lanfear and Thorpe, *ibid*, p. 2865) it appeared probable that increasing the atomic volume of the alkyl group R in the 1-alkylaminobenzthiazole system (X⇌XI) would increase the stability of the *two-membered heterocyclic ring* N=C, of the aminothiazole phase (X) and thus

enhance this phase of the tautomeric system (compare Packer and Thorpe, *J. Chem. Soc.*, 1926, p. 1208). Consequently on ascending the homologous series of 1 alkylaminobenzthiazoles, a gradual shift of equilibrium in favour of the phase (X) would be expected.



(X) (XI)

The nuclear nitrogen atom of the aminothiazole phase (X) has more residual affinity than the corresponding nitrogen atom of the iminodihydro-phase and hence, on increasing the bulk of the alkyl group R, a corresponding increase in the unsaturation of the thiazole nucleus should ensue, leading to an increase in the stability of the bromo-addition compound of the 1-alkylaminobenzthiazole.

At the time of writing these papers, it was erroneously supposed that the bromo-addition compounds of the 1-alkylaminobenzthiazoles obtained from the bromination of *sym.*-arylalkylthiocarbamides in chloroform were *true* benzthiazole bromides (*loc. cit.*), and when qualitative experiments indicated that an increase in "unsaturation" results on ascending a homologous series of 1-alkylaminobenzthiazoles, it appeared that confirmation to the hypothesis just outlined had been obtained. It has now been conclusively proved, however, that the bromo-addition compounds obtained by the bromination of arylthiocarbamides in chloroform, are invariably *hydroperbromides* of the corresponding alkylaminobenzthiazoles, and the original suggestions regarding the increase in unsaturation on ascending a homologous series of 1-alkylaminobenzthiazoles must be considered to be invalid.

Nevertheless, it appeared possible that an increase in stability due to the causes elaborated above, might be observed on increasing the volume of the alkyl group in a series of 1-alkylaminobenzthiazole dibromides, and several attempts were therefore made to determine the stability of a series of 5-chloro-3-bromo-1-alkylaminobenzthiazole dibromides by quantitative methods.

Unfortunately, all attempts to measure the stability of these compounds by hydrolysis, conductivity, and colorimetric methods, proved unsuccessful.

It appeared to us possible, however, that an investigation of the thermal dissociation of the compounds, $NBr_2 \rightleftharpoons N + Br_2$, on the lines on which Ephraim (*Ber.*, 1917, 50, 1069) has investigated the alkali perhalides, might furnish the desired information. Actually,

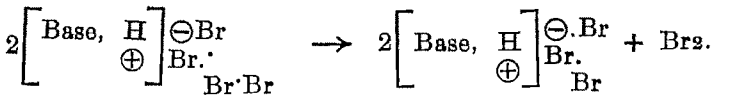
however, the alkylaminobenzthiazole dibromides behaved quite differently from the compounds described by Ephraim and betrayed no appreciable dissociation pressure until within about 20° of their melting point, when decomposition commenced rapidly, and proceeded steadily with no evidence of an equilibrium of the type which we had anticipated.

Although the original object of the research was therefore not attained these experiments nevertheless removed any doubt which might be entertained regarding the nature of the benzthiazole dibromides being that of *true compounds.*

Apparent confirmation of an increased tendency for alkylaminobenzthiazoles to form hydroperbromides, was obtained from a study of the bromination of the sym-o-*tolylalkylthiocarbamides.* It was observed that the methyl, ethyl, and *n*-propyl homologoues gave rise to *hydrotetrabromides* of the corresponding 1-alkylamino-3-methylbenzthiazoles, whilst sym-o-*tolyl*-n-*butyl*, -iso*butyl*-, -n-*amyl*-, -iso*amyl*-, -n-*hexyl*-, and n-*heptyl-thiocarbamides* yielded *hydrohexabromides* of the corresponding bases.

The hydrohexabromides in question were strikingly unstable and since it is apparently impossible to obtain absolute evidence that these unstable substances are *not* solid solutions of bromine and a hydroperbromide of a lower order, we prefer not to attempt to base far reaching conclusions on the results of such experiments. It is at least possible, that the production of such complexes is intimately connected with the solubilities of the components concerned.

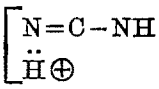
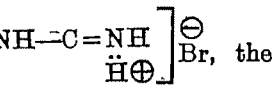
The problem of the structure of the even-numbered hydroperbromides of the aminobenzthiazoles (3, 7, 8, 9, 10, 11, 12, 13) is of considerable importance, because the stability of certain members of the group, such as the hydrodibromide of 1-aminobenzthiazole and the hydrotetrabromide of 1-*p*-toluidino-5-methylbenzthiazole, together with their formation under different conditions, indicates that the substances are *true* compounds (Hunter, *J. Chem. Soc.*, 1930, p.125). The fact that they can be prepared from solutions of the hydrobromides of the bases in inert solvents and bromine (*loc. cit.*) suggests that their structures may contain the hitherto unknown $Br_2^{\ominus}$ and $Br_4^{\ominus}$ ions ; the general formulae of the compounds being, $[Base, H]^{\oplus}Br_n^{\ominus}$. On such a basis, the ready elimination of bromine from 1-anilinobenzthiazole hydrotetrabromides with the production of stable hydrotribromides, can be interpreted on the generally accepted view that singlet linkages derive stability from mutual association :



The main difficulty which presents itself in relation to such a hypothesis is, of course, the formulation of the even-numbered hydroperbromides as odd-electron molecules.

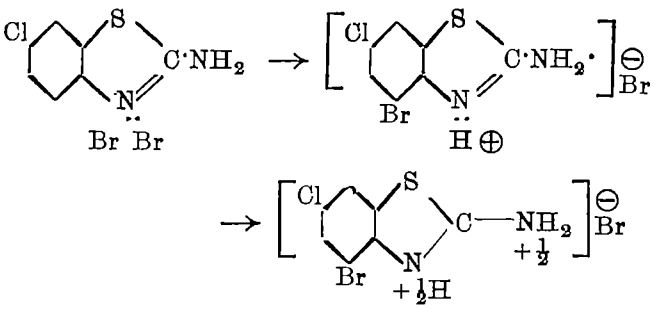
Another topic which arises in connection with the hydroperbromides of the aminobenzthiazoles is the observation that the bromination of a single arylthiocarbamide may sometimes give rise to two apparently isomeric forms of the hydroperbromide of the corresponding aminobenzthiazole (7, 10).

At the time when the first observations of this phenomenon were recorded (1926), it was supposed that the bromo-addition compounds in question were true benzthiazole bromides, and it was suggested that they might be derived from the tautomeric forms of the amidine system, and possess structures of the type, $N[H]Br_2:C:NX$ and $NBr_2:C\cdot N[H]X$. Since it is now known that the bromo-addition compounds in question are hydroperbromides, this hypothesis is obviously invalid. Nevertheless, careful reinvestigation of one of these cases, that of the hydrotribromide of 1-amino-5-methylbenzthiazole (7), confirms the statements which were made by one of us with regard to it nearly five years ago. There *are* two forms of this hydrotribromide, but we have found that on keeping one of them in contact with the liquid phase from which it originally crystallises, that it redissolves, giving a solution from which the second, and more stable, form crystallises. The phenomenon therefore appears to be merely one of a metastable equilibrium of the type which has already been described by Chattaway and Lambert (*J. Chem. Soc.*, 1915, **107**, 1766) in connexion with *p*-bromoacetanilide and 2 : 4-dibromoacetanilide.

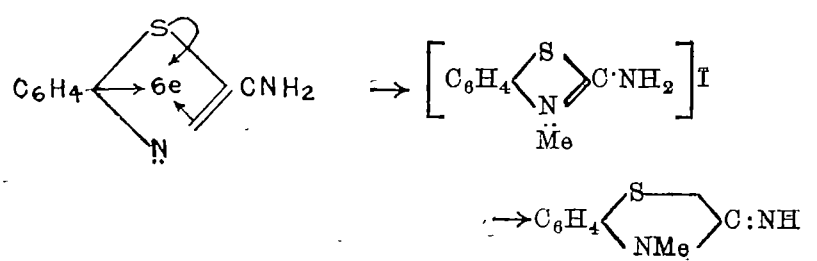
Regarding the possibility of the existence of isomeric hydrobromides (or hydrotribromides) of the type,  and  , the observation of Burtles and Pyman (*J. Chem. Soc.*, 1923, **123**, 362) that both 2 : 4- and 2 : 5-diphenylglyoxaline give rise to identical salts indicates that the anions of the tautomers are electromeric. The simplest view, and the one which was suggested to us by Professor Ingold (*private communication*)

is that the positive charge produced by conversion of an amidine into the ammonium condition is located to the extent of about a half charge on each nitrogen atom, just as the negative charge is divided in the carboxylate ion; the ion of asymmetrical triad system being therefore symmetrically constituted quite generally.

A full interpretation of the migration of bromine into the nucleus in a benzthiazole dibromide might therefore be visualised for the case of the 5-chloro-1-amino-compound described in this paper as follows:

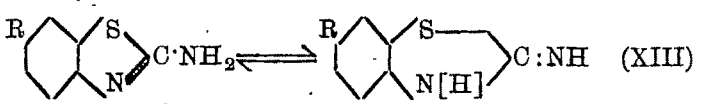


A study of the mobility of the symmetrical triad system [H]N —C:N⇌N:C·N[H] in 1 aminobenzthiazoles indicates plainly that the dominating factor is the aromatic character of the heterocyclic nucleus. Bases of this type (XIV⇌XV, R=H) methylate almost exclusively on the nuclear nitrogen atom (7, 14, 16, 17, 18) yielding iminomethyldihydro derivatives (compare also Young and Crookes, *J. Chem. Soc.*, 1906, **89**, 59), and it may be noted that Tschitschibabin and Konowalowa have recorded similar observations in connexion with the α-aminopyridines (*Ber.* 1921, **54**, 814). These facts are clearly capable of interpretation on the basis of the sextuple group theory to which we have already alluded (p. 148). In 1-aminobenzthiazole, for instance, the sextuple group is completed without calling on the lone pair of electrons of the nuclear nitrogen atom which are therefore available for methiodide formation, leading to the production of the hydriodide of 1-imino-2-methyl-1:2-dihydrobenzthiazole.



Destruction of the aromatic character of the heterocyclic nucleus causes enhanced activity in the iminodihydro-form, resulting in the formation of methylamino-derivatives (Young and Crookes, *loc. cit.* ; compare Forsyth and Pyman, *J. Chem. Soc.*, 1926, p. 2502).

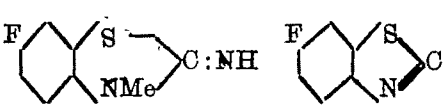
In a recent investigation (19) a study was made of the effect of polar substituents on the methylation of certain 5-substituted-1-aminobenzthiazoles (XII⇌XIII), in which the *para*-substituent to the nuclear nitrogen atom can act by virtue of electronic displacements, partly similar to those which operate in aromatic substitution (Ingold, Shoppee, and Thorpe, *J. Chem. Soc.*, 1926, p. 1477). It was found that the nitro-, chloro-, bromo-, ethoxy-, and methyl bases (R=NO_2, Cl, Br, OEt, and Me respectively) reacted exclusively in the aromatic phase yielding iminomethyldihydrobenzthiazoles.

(XII)  (XIII)

Particular interest attaches itself to the mobility of *5-fluoro-1-aminobenzthiazole* (XII⇌XIII, R=F) and we therefore directed our attention to the rational synthesis of this base from *p*-fluoroaniline.

Thiophosgenation of the fluoroaniline gave rise to the corresponding *thiocarbimide*, which yielded *p-fluorophenylthiocarbamide*, on condensation with ammonia ; bromination of this compound under conditions similar to those employed in the case of the chlorine and bromine analogues, gave an excellent yield of the required *fluorobenzthiazole*.

Methylation of 5-fluoro-1-aminobenzthiazoles with methyl sulphate proved to be quite analogous to that of the other 5-substituted-1-aminobenzthiazoles previously investigated (19) ; the only isolable product being *5-fluoro-1-imino-2-methyl-1:2-dihydrobenzthiazole* (XIV). The presence of the isomeric *5-fluoro-1-methylaminobenzthiazole* (XV), which was synthesised from sym-p-*fluorophenylmethylthiocarbamide* and bromine, could not be detected in the methylation product.

(XIV)  (XV)

Now, it has been pointed out by Ingold and Ingold (*J. Chem. Soc.*, 1928, p. 2254) that if considerations relating to the inductive

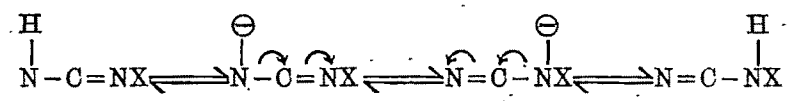
and directive effects (Ingold and Shaw, *J. Chem. Soc.*, 1927, p. 2918 ; Ingold and Vass, *J. Chem. Soc.*, 1928, p. 417) are taken as indicating the electrical states of atoms, the sequence F>Cl>Br>I should connote the order of negativity of halogen substituents in corresponding compounds; in other words, the degree of pre-formation of halide ions. In reactions which involve the separation of a halide ion, however, the actual reactivities of the benzyl halides are in opposite order to that which would be expected from a consideration of the effects of halogens on nuclear substitutions. In view therefore of their suggestion, that the primary condition affecting the reactivity of halogen substituents is not so much the *average* electrical condition of these atoms, but rather the extent to which they are capable of *temporary* electrical polarisation by external fields of reagent molecules, it appeared desirable to examine the behaviour of the remaining 5-halogen--1-aminobenzthiazole (XVI⇌XVII, R=I) under conditions as closely identical as possible to those employed in the case of the fluorine derivative.

5-Iodo-1-aminobenzthiazole on methylation with methyl sulphate, yielded solely the iminomethyldihydro-*derivative* (XIV, with I in place of F), unaccompanied by the 5-iodo-1-methylamino-*compound* (XV, with I in place of F), which was synthesised from sym-p-*iodophenylmethylthiocarbamide*.

Considerable interest attaches itself to the application of modern electronic theories to the tautomerism of systems, whose mobility depends on the presence of a hydrogen atom and an appropriately situated double bond. The first definite correlation of the behaviour of highly mobile systems of the glutaconic type with the reversible isomeric changes which take place in Fittig's unsaturated acids in the presence of a large concentration of hydroxyl ions, was made by Professor J. F. Thorpe (*J. Chem. Soc.* 1923, **123**, 1361) in an introduction to the series of papers which have been published by Kon and his collaborators on the so-called "three-carbon system." The extension of such principles to other mobile triad systems follows largely as a matter of course.

The application of the general principles of cationotropy (Lapworth, *J. Chem. Soc.*, 1901, **79**, 1265 ; Ingold, *Annual Reports of the Chemical Society*, 1927, p. 106) to the amidine system, necessitates that the first condition for mobility should be that the mobile hydrogen atom (proton) first dissociates from the unsaturated molecule, leaving an electromeric anion, $\overset{\ominus}{N}-C=N\dot{X}$, in which tautomeric

electronic displacements $\overset{\curvearrowright}{N}-\overset{\curvearrowright}{C}=NX$, bring about a redistribution of the negative charge between the two nitrogen atoms, the eliminated proton having thereby two points of recombination. The complete picture for the tautomerism of the amidine system being



The tendency for an amidine system to come into equilibrium under given conditions should on the basis of this theory, therefore, depend on the stability of the anion in which the actual isomeric change takes place. The *equilibrium* should therefore depend on the stability of the anion $\overset{\ominus}{N}-C=NX$ relative to its isomer, $N=C-\overset{\ominus}{N}X$, and also on the stability of the covalency linkages by means of which the proton is to re-associate with these anions in the $\alpha\beta$- and $\beta\gamma$-molecules.

In the three carbon system, $[H]C{\cdot}C:C\rightleftharpoons C:C{\cdot}C[H]$, present in indene (Ingold and Piggott, *J. Chem. Soc.*, 1920, **123**, 1470) and in the pentad keto-enol system, $[H]C{\cdot}C:C{\cdot}C:O\rightleftharpoons C:C{\cdot}C[H]C:O$, studied by Kon and Linstead and their pupils (*J. Chem. Soc.*, 1925, **127**, 616; 1927, pp. 262, 2579; 1928, p. 2343; *et.seq.*), there is no doubt that the mobile hydrogen atom is acidic, and that the ability of substituents to promote prototropic change runs more or less parallel with their degree of electron attraction power as deduced from their directive effect in aromatic hydrogen substitutions (Ingold, Shoppee, and Thorpe, *J. Chem. Soc.*, 1928, p. 1477).

An important distinction which is often overlooked in connexion with this correlation of the ability of a group to promote prototropic change with its *meta*-orienting power in benzene substitution (Linstead, *J. Chem. Soc.*, 1929, p. 2498), is that which exists between the *polarisation* of a molecule and its *polarisability*, and we wish to take this opportunity to give emphasis to Shoppee's explanation of the position (*J. Chem. Soc.*, 1930, p. 969). Benzene hydrogen substitutions clearly depend on the negative character of the electrical field at the point of the attaching reagent, whereas tautomeric changes involving a mobile hydrogen atom should on the basis of the cationotropic theory, depend on the positivity of the field at the centre of ionisation. The necessary condition which is required for the former, is one which can arise from the permanent

polarisation of the aromatic molecule due to the electron repulsion of the substituent, or from the molecular *polarisability* of the compound which is enhanced by the presence of substituents containing unshared electrons. In the case of a substituent which attracts electrons, polarisation will have a *deactivating* effect because it causes a decrease of electron availability at the point of the reaction. On the other hand, polarisability due to the presence of a substituent capable of sharing additional aromatic electrons in a molecule in which a free path for electron transference is present, will *not* produce any deactivation because displacements of this type would lead to a recession of electrons from the seat of the reaction. Now the electron recession necessary for the positivity at the field of ionisation on which mobile hydrogen tautomerism is assumed to depend can arise in two ways: (*i*) from polarisation due to the electron attraction of the substituent, or (*ii*) from the polarisability which results from the presence of a substituent which is capable of sharing unshared electrons possessed by the system. An electron-repelling substituent will therefore have a retarding influence because it tends to oppose the production of positivity at the point of ionisation, whereas polarisability which results from the presence of a substituent containing unshared electrons which can be shared with the system, will not lead to electron displacements because they would involve electron-accession to the point of ionisation for which, there is no demand.

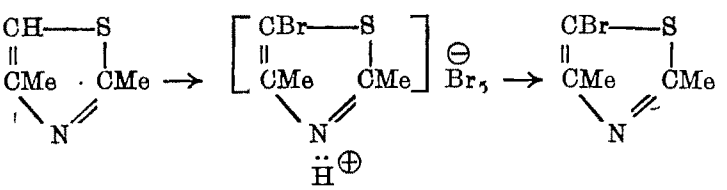
Retardation of aromatic hydrogen-substitution does not necessarily run parallel with facilitation of prototropy, and therefore an agreement of the type expected by Linstead (*loc. cit.*) for the effect of groups such as, CN, COMe, and CO_2Et, on the mobility of the pentad-keto-enol system and their *meta*-directive power, is not to be anticipated.

The acidity of the simpler amidines, which is sufficient to allow of the formation of definite metallic salts, accords well with the cationotropic theory which we have discussed. On the other hand, it seems a little difficult to reconcile the lack of acidity of semi-cyclic amidines containing a heterocyclic nucleus, of the type we have been studying during the last six years, with the relatively high mobility which they exhibit in the symmetry tests. As has already been pointed out (19), a typical member of the series, such as 1-amino-5-methylbenzthiazole can be heated with sodium in xylene for hours, without any evidence of the formation of a sodio-deriva-

tive of the expected type. It must, of course, be conceded that the polar field offered by this solvent, as indicated by its dielectric constant, is very low, but it is intended to investigate this question more fully at an early date.

Now, the whole of the investigations which have previously been carried out in connexion with the unsaturation and tautomeric mobility of thiazoles, have dealt with benzthiazole and napthathiazole derivatives. It was therefore of interest to extend the present investigation to certain simple thiazole derivatives, in which the complication of aromatic conjugation from a benzene or naphthalene ring does not arise, and certain preliminary experiments on these lines are included in the experimental portion of this paper.

In the first place it was desirable to investigate the bromination of a typical thiazole base which was free from aromatic substituents, and 2:4-dimethylthiazole (XVI) was chosen for this purpose. This base behaved in quite a different manner from our expectations, however, and gave rise to an unstable *hydropentabromide* of a monobromosubstitution derivative, without any evidence of the formation of a true thiazole bromide. From the properties of this monobromo-*base* which was obtained by reduction of the hydropentabromide with sulphurous acid, there is little doubt that it is *5-bromo-2:4-dimethylthiazole* (XVIII), and that the hydropentabromide is therefore represented by a formula (XVII).



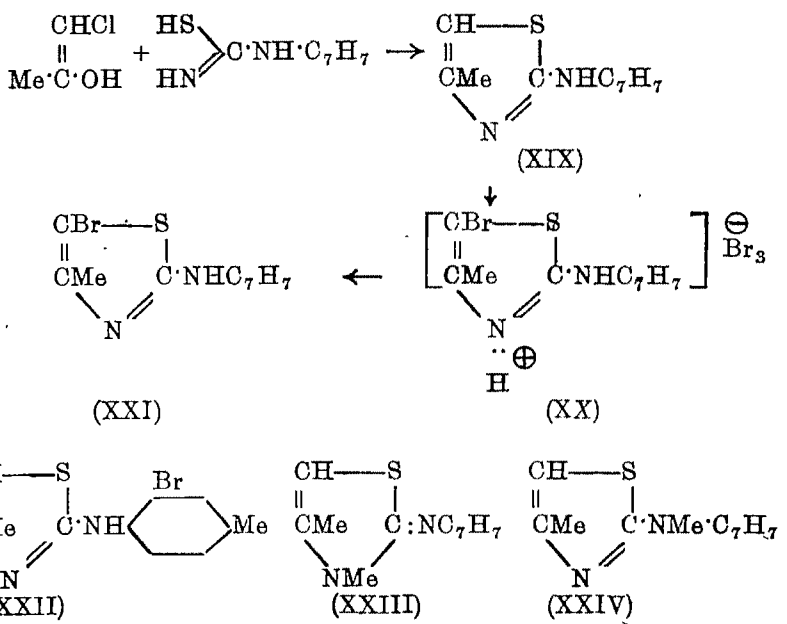
(XVI) (XVII) (XVIII)

Attention was next directed to the bromination and methylation of a typical semi-cyclic amidine containing the thiazole ring, and 2-*p*-toluidino-4-methylthiazole (XIX) was chosen for this purpose. In view of the doubt which has been cast by Tcherniac (*J. Chem. Soc.*, 1919, **115**, 1071) on many of Hantzsch's thiazole syntheses from thiocyanoacetone (*Annalen*, 1888, **249**, 7; compare also Hantzsch and Weber, *Ber.*, 1887, **20**, 3118), the *p*-toluidinothiazole was rationally synthesised from *p*-tolylthiocarbamide and monochloroacetone. The base obtained in this way answered very closely to the description of the compound given by Hantzsch, although we succeeded in

raising the m.p. of the compound 2 or 3 degrees above that recorded in the literature.

On bromination in chloroform at low temperature, it yielded a beautifully crystalline *hydrotribromide* of a monobromosubstitution derivative. The monobromosubstitution *base* obtained by reduction with sulphurous acid, is assumed to be 5-*bromo*-2-p-*toluidino*-4-*methylthiazole* (XXI) on account of its non-identity with 2-o-*bromo*-p-*toluidino*-4-*methylthiazole* (XXII), which was synthesised for comparative purposes from *o*-bromo-*p*-tolylthiocarbamide and chloroacetone.

Methylation of 2-*p*-toluidino-4-methylthizole (XIX) yielded solely 2-p-*tolylimino*-3:4-*dimethyl*-2:3-*dihydrothiazole* (XXIII), which was also synthesised from sym.-*p*-tolylmethylthiocarbamide and monochloroacetone. The presence of the isomeric 2-p-*tolylmethylamino*-4-*methylthiazole* (XXIV) which was prepared from as-*p*-tolylmethylthiocarbamide and chloroacetone, could not be detected in the methylation product. The preferential elimination of hydrogen attached to the NMe-group of the thiocarbamide as water, in conjunction with the hydroxyl group of the enolic form of the chlorinated ketone in the former condensation, seems noteworthy.

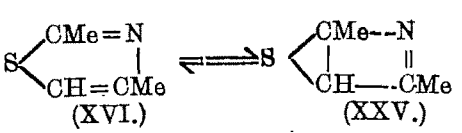


This result produces a striking contrast (compare also Young and Crookes, *loc. cit.*) to the behaviour of 1-anilinobenzthiazole, which

yields a mixture of 1-phenylimino-2-methyl-1:2-dihydrobenzthiazole and 1-phenylmethylaminobenzthiazole in the approximate proportion of 2:1, on methylation (19). From the point of view of methylation therefore, the attraction of the aromatic nucleus on the $\alpha\beta$-double bond is therefore considerably less in the case of the 2-arylamino-thiazoles than in that of the 1-anilinobenzthiazoles.

The suggestion may therefore be offered that a certain degree of the aromatic character of the thiazole nucleus is lost when it is combined with a benzene ring, as in benzthiazole. Since benzthiazole is a dihetero-derivative of naphthalene, this would appear to constitute another example of the mutual effect of aromatic nuclei such as is seen in naphthalene itself, where neither of the presumably identical homocyclic carbon rings exhibits full benzenoid characteristics until one of them is reduced, as in the tetrahydro-derivative (Bamberger, *Annalen*, 1890, **257**, 1; compare Challenor and Ingold, *J. Chem. Soc.*, 1923, **123**, 2066). This receives support from the bromination experiments described in this paper, since the thiazole derivatives exhibit no apparent tendency towards the formation of addition products, but pass directly into bromo-substitution derivatives, while benzthiazoles tend to yield addition products, prior to nuclear substitution.

If intra-annular tautomeric interchanges of the type which have been postulated by Ingold in the case of the benzene nucleus (*J. Chem. Soc.*, 1922, **121**, 1133, 1143; 1923, **123**, 2081), are indeed responsible for the manifestation of the characteristic properties of aromatic compounds, it is clear that they must find their counterpart in heterocyclic compounds of the type of thiophen, pyridine, and thiazole (compare Ingold, *J. Chem. Soc.*, 1924, **125**, 87). It might be anticipated, for instance, that 2:4-dimethylthiazole would possess a dual set of properties in accordance with its double bonded formula (XVI) which follows from its synthesis from thioacetamide and monochloroacetone, and the bridged structure (XXV) which is the analogue of the Dewar phase of the aromatic nucleus.

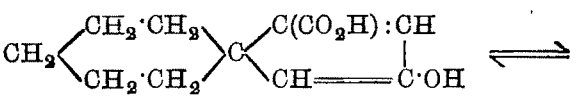


(XVI.) (XXV.)

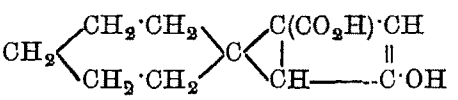
Actually, however, the experimental investigation of this problem presents great difficulty. It is, for instance, quite out of question to hope to obtain evidence of the two structures from a study of the

regulated oxidation of the base by reagents such as potassium permanganate and potassium ferricyanide, which have been used with such success in the case of the five-carbon intra-annular nucleus (Farmer, Ingold, and Thorpe, *J. Chem. Soc.*, 1922, **121**, 128) because the attack of the oxidising reagent commences at the sulphur atom (compare Reissert and Manns, *Ber.*, 1928, **61**, 1308). Experiments are, however, in progress which have for their object the synthesis of the bridged phase of 2:4-dimethylthiazole (XXIX), although it is anticipated that such a substance would prove to be identical with the dimethylthiazole described in the Experimental.

The facile substitution of bromine for hydrogen on the carbon atom 5 in 2:4-dimethylthiazole is of interest in this connexion, because this is the position which corresponds to that of substitution by bromine in 5-*cyclo*hexane*spirodicyclo*-$\triangle^2$-penten-3-ol-1-carboxylic acid (XXVI$\rightleftharpoons$XXVII), in which the *cyclo*hexane ring is assumed to have decreased the stability of the bridge bond in the phase (XXVII) (Ingold and Thorpe, *J. Chem. Soc.*, 1919, **115**, 320) to the point where it approaches that of the para-bridge in the Dewar phase of the aromatic nucleus (Ingold, Seeley, and Thorpe, *J. Chem. Soc.*, 1923, **123**, 853).



(XXVI)



(XXVII)

Experimental.

The Synthesis of 1-Alkylamino-5-methylbenzthiazoles from sym-*p-Tolylalkylthiocarbamides and the Conversion of these Bases into the Hydrotribromides of 3-Bromo-1-alkylamino-5-methylbenzthiazoles.*—sym-Di-*p*-tolylthiocarbamide was prepared in 80—90 % yield by heating a mixture of *p*-toluidine (450 g.), alcohol (600 c.c.), carbon disulphide (700 c.c.), and potassium hydroxide (50 g.) on a steam bath, under an efficient reflux for 8 hours.

p-Tolylthiocarbimide was prepared by heating quantities of 50 g. of the di-*p*-tolylthiocarbamide with acetic anhydride (60 c.c.) at the b.p. of the mixture for *one* minute and pouring the hot liquid into

warm water; the thiocarbimide being isolated by distillation in steam in the usual way. The colourless and highly refractive oil obtained in this way, solidified on cooling to a mass of transparent prisms, which were purified by being melted over anhydrous calcium chloride and distilling the product under reduced pressure. In this way, 200 g. of pure *p*-tolylthiocarbimide, b.p. 140°/34 mm., were obtained from 440 g. of sym-di-*p*-tolylthiocarbamide. When the time of heating with acetic anhydride was allowed to exceed one minute, poor yields were obtained owing to the decomposition of the thiocarbimide into carbonyl sulphide and *p*-acetyltoluidine (Werner, *J. Chem. Soc.*, 1891, **59**, 396).

sym-p-*Tolylethylthiocarbamide* was prepared by adding 10 c.c. of a 33% solution of ethylamine in water to a boiling solution of 10 g. of *p*-tolylthiocarbimide in alcohol (50 c.c.), the mixture being heated for a few minutes at its boiling point. On cooling, the *thiocarbamide* separated and on recrystallisation from dilute methyl alcohol, formed thin colourless plates, m.p. 97°. (Found: N, 16·3. $C_{10}H_{14}N_2S$ requires S, 16·5 per cent.). Yield: 12 g.

1-*Ethylamino*-5-*methylbenzthiazole Hydrotetrabromide*.—A suspension of 2 g. of *p*-tolylethylthiocarbamide in chloroform (15 c.c.) was treated with bromine (3·3 c.c. in 15 c.c. of the same solvent) and the mixture was heated on a steam-bath, under reflux, for 15 minutes when hydrogen bromide was copiously evolved. The warm solution was rapidly filtered, cooled in a vacuum desiccator and slightly concentrated under reduced pressure at laboratory temperature, when the *hydrotetrabromide* crystallised in glistening red needles, which were rapidly dried on porous earthenware in a vacuum over potassium hydroxide. The tetrabromide melted with decomposition at 78°. [Found: Br (total), 62·2; Br (labile), 47·0, $C_{10}H_{12}N_2S,HBr(Br_3)$ requires Br (total), 62·5; Br (labile), 46·9 per cent.].

1-*Ethylamino*-5-*methylbenzthiazole*.—The bromo-addition compound was suspended in sulphurous acid and treated with sulphur dioxide until reduction was complete; the mixture was basified with ammonia and the *ethylaminobenzthiazole* was recrystallised from methyl acohol. The base formed colourless flat prisms, m.p. 129°. (Found: S, 16·3. $C_{10}H_{12}N_2S$ requires S, 16·7 per cent.).

Bromination.—A solution of 2 g. of the ethylaminobenzthiazole in chloroform (30 c c.) was treated with bromine (3·3. c.c. in 10 c.c. of chloroform), and the solution was kept. 3-*Bromo*-1-*ethyl*-

amino-5-methylbenzthiazole hydrotribromide crystallised in yellow needles which had m.p. 147° (darkening with sintering at 130-40°), after being dried in a vacuum. [Found: Br (total), 62·6; Br (labile), 32·0. $C_{10}H_{11}N_2BrS$, $HBr(Br_2)$ requires Br (total), 62·5; Br (labile), 31·3 per cent.]. *3-Bromo-1-ethylamino-5-methylbenzthiazole* obtained either by reduction of the hydrotribromide with sulphurous acid, or by boiling this bromo-addition compound with alcohol, separated from ethyl acetate in prisms, m.p. 150°. (Found: Br, 29. $C_{10}H_{11}N_2BrS$ requires Br, 29·5 per cent.).

sym-p-*Tolyl*-n-*propylthiocarbamide*.—*n*-Propylamine (8 c.c.) in water (25 c.c.) was added to a hot solution of *p*-tolylthiocarbimide (10 g.) in alcohol (50 c.c.) and the mixture was heated for a few minutes on a steam-bath. The *propylthiocarbamide* separated on cooling, and a further quantity was obtained by working up the mother-liquors. On recrystallisation from dilute alcohol, the thiocarbamide formed colourless plates, m.p. 70°. (Found: S, 15·6. $C_{11}H_{16}N_2S$ requires S 15·4 per cent.). Yield: 13 g.

1-n-*Propylamino-5-methylbenzthiazole Hydrotetrabromide*.—A solution of 2 g. of the propylthiocarbamide in chloroform (15 c.c.) was treated with bromine (3·1 c.c. in 15 c.c. of chloroform) and the mixture was heated under reflux for 15 minutes. The *hydrotetrabromide* crystallised in small orange needles which were dried in a vacuum; m.p. 61°. (Found: Br, 61·1. $C_{11}H_{14}N_2S$,$HBr(Br_3)$ requires Br, 60·8 per cent.). 1-n-*Propylamino-5-methylbenzthiazole* separated from methyl alcohol in transparent flat, hexagonal prisms, m.p. 116°. (Found: S, 15·3. $C_{11}H_{14}N_2S$ requires S, 15·5 per cent.).

3-Bromo-1-n-*propylamino-5-methylbenzthiazole Hydrotribromide*.—A solution of bromine (3·1 c.c.) in chloroform (10 c.c.) was added to 2 g. of the *n*-propylaminobenzthiazole in the same solvent (26 c.c.) and the solution was concentrated under reduced pressure at laboratory temperature. An unstable, red, hydroperbromide separated, which decomposed yielding the *hydrotribromide*, on being kept in a vacuum over potassim hydroxide overnight. This hydrotribromide formed yellow prisms, m.p. 130° (decomp.). [Found: Br (total), 60·4; Br (labile), 30·6. $C_{11}H_{13}N_2BrS$,$HBr(Br_2)$ requires Br (total), 60·8; Br(labile), 30·4 per cent.].

3-Bromo-1-n-*propylamino-5-methylbenzthiazole* separated from alcohol in prisms, m.p. 116°. (Found: Br, 28·3. $C_{11}H_{13}N_2BrS$ requires Br, 28·1 per cent.).

sym-p-*Tolyl*i*sobutylthiocarbamide*, prepared from the tolylthiocarbimide and *iso*butylamine, separated from dilute methyl alcohol

in glistening plates, m.p. 87°. (Found: S, 14·5. $C_{12}H_{18}N_2S$ requires S, 14·4 per cent.).

1-iso*Butylamino-5-methylbenzthiazole Hydrotribromide*.—A solution of the *iso*butylthiocarbamide (2 g.) in chloroform (15 c.c.) was treated with bromine (2 c.c. in 15 c.c. of chloroform) and the mixture was heated under reflux for 15 minutes. Concentration of the solution in *vacuo* yielded orange-yellow plates of the *hydrotribromide* of the butylaminobenzthiazole, m.p. 89° (decomp.). [Found: Br (total), 52·3; Br (labile), 31·3. $C_{12}H_{16}N_2S,HBr(Br_2)$ requires Br (total), 52·3; Br (labile), 34·7 per cent.].

1-iso*Butylamino-5-methylbenzthiazole* crystallised from methyl alcohol in stellate clusters of thin oblong prisms, m.p. 132°. (Found: S, 14·1. $C_{12}H_{16}N_2S$ requires S, 14·5 per cent.).

3-*Bromo*-1-iso*butylamino-5-methylbenzthiazole Hydrotribromide*, prepared by concentrating the solution obtained from the butylaminobenzthiazole (2 g.), chloroform (30 c.c.) and bromine (2·9 c.c.), under reduced pressure at laboratory temperature, formed yellow prisms, m.p. 126° (decomp.). [Found: Br (total), 59·1; Br (labile), 30·9. $C_{12}H_{15}N_2BrS$, $HBr(Br_2)$ requires Br (total), 59·3; Br (labile), 29·7 per cent.].

3-*Bromo*-1-iso*butylamino-5-methylbenzthiazole* crystallised from methyl alcohol in prisms, m.p. 95°. (Found: S, 27·0. $C_{12}H_{15}N_2BrS$ requires Br, 26·8 per cent.).

Bromination of p-*Tolylthiocarbamide*.—A suspension of 2 g. of *p*-tolylthiocarbamide in chloroform (15 c.c.) was treated with bromine (4 c.c. in 15 c.c. of chloroform) and the the mixture was heated on a steam-bath, under reflux, for 15 minutes. On cooling the solution in a vacuum, deep red crystals of a highly unstable substance separated, whose m.p. could not be determined on account of its rapid decomposition. (Found: Br, 65·1. $C_8H_8N_3SBr(Br_3)$ requires Br, 66·1 per cent.). On keeping in a vacuum, this substance yielded the orange-yellow *hydrotribromide*, m.p. 108-109° (sintering at 100°) already recorded (Hunter, *loc. cit.*). (Found: Br, 59·5. Calc. Br, 59·2 per cent.). If, however, the deep red crystals first obtained were allowed to remain in contact with the mother-liquor for several hours, exposed to moist laboratory air, they redissolved and the liquid subsequently deposited deep orange-red crystals of the *second* form of the *hydrotribromide*, m.p. 133°. [Found: Br (total) 59·6; Br (labile), 39·7. Calc. Br (total), 59·2; Br (labile), 39·5 per cent.].

The Synthesis of 5-Chloro-1-alkylaminobenzthiazoles from sym-*p-Chlorophenylalkylthiocarbamides: the Conversion of these Bases into Hydroperbromides of the 5-Chloro-3-bromo-1 alkylaminobenzthiazoles, and the Preparation of a Series of 5-Chloro-3-bromo-1-alkylaminobenzthiazole Dibromides.*—Several methods of preparation of *p*-chloroacetanilide have been described in the literature, but in all cases the yields are poor. We are indebted to Professor R. W. West for the following method of preparation, which was used in connexion with the present investigation.

A solution of 400 g. of acetanilide in a mixture of glacial acetic acid (150 c.c.) and concentrated hydrochloric acid (500 c.c.) was cooled to 0° in a large enamelled pan, surrounded by an efficient freezing mixture. The filtrate obtained from shaking a mixture of 600 g. of bleaching powder with water (4000 c.c.) at intervals of a period of time greater than an hour, was then added gradually to the cooled mixture, which was mechanically stirred during the addition, which occupied several hours. The temperature of the chlorination was kept below 5°, and the white crystals which separated were collected and dried at 100°. The yield of crude *p*-chloroacetanilide was 225 g.

A mixture of this product (450 g.) and concentrated hydrochloric acid (1200 c.c.) was heated under reflux for 2 hours, cooled, and neutralised with anhydrous sodium carbonate; the *p*-chloroaniline was isolated by distillation in steam, when it formed a colourless oil which solidified on cooling. Yield: 265 g.

sym-Di-*p*-chlorophenylthiocarbamide was prepared by heating a mixture of *p*-chloroaniline (365 g.), carbon disulphide (700 c.c.), alcohol (600 c.c.), and sulphur (20 g.) (compare Hugershoff, *Ber.*, 1899, **32**, 2245) under reflux for 3 hours. Yield: 400 g.; m. p. 171°.

p-Chlorophenylthiocarbimide was prepared in 80% yield by heating quantities of 100 g. of sym-di-*p*-chlorophenylthiocarbamide with acetic anhydride (110 c.c.) under reflux, for 30 minutes, pouring the mixture into hot water and isolating the thiocarbimide by distillation in steam. The chlorophenylthiocarbimide distilled over as a colourless oil, which solidified on cooling. On recrystallisation from methyl alcohol it formed slender white needles, m. p. 45°, having a pronounced aniseed-like odour.

In connexion with the present investigation, we found that 3·1 kg. of acetanilide gave 250 g. of *p*-chlorophenylthiocarbimide; the over-all yield for the process is therefore only 6·4 per cent.

The 5-chlorobenzthiazoles were prepared on lines similar to those described in connexion with the 1-alkylamino-5-methylbenzthiazole derivatives.

5-Chloro-1-aminobenzthiazole Hydrodibromide.—This compound, previously described as a dibromide by Dyson, Hunter, and Morris (12), was prepared by bromination of a suspension of 2 g. of *p*-chlorophenylthiocarbamide in chloroform (15 c.c.) with bromine (3·4 c.c. in 15 c.c. of the same solvent). It formed aggregates of silky, red-brown needles, which lost bromine at 80-90°, showed softening at 130° and melted with charring at 230-235°. [Found: Br (total), 45·9; Br (labile), 24·0. Calc. for $C_7H_5N_2ClS,HBr(Br)$: Br (total), 46·4; Br (labile), 23·2 per cent.].

Bromination of 5-Chloro-1-aminobenzthiazole.—A suspension of 2 g. of the 5-chloro-1-amino-base in chloroform (50 c.c.) was treated with bromine (3·4 c.c. in 15 c.c. of the same solvent), and the liquid was rapidly filtered and kept in an evacuated desiccator, when silky orange needles, having the composition of a *dibromide* separated, m. p. 82-83°. (Found: Br, 46·7. $C_7H_5N_2Br_2S$ requires Br, 46·4 per cent.). Attempts to dissolve this bromo-addition compound in chloroform resulted in a rapid discharge of colour, accompanied by conversion into the *hydrobromide* of 5-chloro-3-bromo-1-aminobenzthiazole (compare Hunter, *J. Chem. Soc.*, 1930, p. 127). When the bromo-addition compound was added to a mixture of chloroform and potassium iodide solution in water, acidified with acetic acid, and the mixture was shaken, an appreciable liberation of iodine was observed. *5-Chloro-3-bromo-1-aminobenzthiazole* separated from ethyl acetate in small needles, m.p. 245°. (Found: Br, 30·2. $C_7H_4N_2ClBrS$ requires Br, 30·4 per cent.)

5-Chloro-3-bromo-1-aminobenzthiazole Dibromide.—A solution of the base in the minimum quantity of warm chloroform was treated with excess of bromine, and the solution was allowed to cool gradually, when the *dibromide* crystallised. This bromo-addition compound was collected, washed with a little chloroform and dried overnight in a vacuum. It formed glistening golden plates, which showed loss of bromine at 160°, but were unmelted at 280°. [Found: Br (total), 56·5; Br (labile), 37·4. $C_7H_4N_2Cl\,BrS(Br_2)$ requires Br (total), 56·7; Br (labile), 37·8 per cent.].

5-Chloro-3-bromo-1-methylaminobenzthiazole Hydrotribromide.—A suspension of 1 g. of 5-chloro-1-methylaminobenzthiazole (19) in 30 c.c. of chloroform was treated with bromine (1·6 c.c. in 15 c.c. of

chloroform). The bromo-addition *compound* formed glistening orange plates, m. p. 270° (with charring; loss of bromine at 200°). (Found: Br, 61·9. $C_8H_7N_2ClBrS,HBr(Br_2)$ requires Br, 61·7 per cent.).

5-Chloro-3-bromo-1-methylaminobenzthiazole separated from ethyl acetate-chloroform in feathery white needles, m. p. 180°. (Found: Br, 29·0. $C_8H_6N_2ClBrS$ requires Br, 28·8 per cent.)

5-Chloro-3-bromo-1-methylaminobenzthiazole dibromide, prepared as in the case of the amino-compound, formed small yellow plates, which charred without melting at 250°. [Found: Br (total), 55·2; Br (labile), 36·5. $C_8H_6N_2ClBrS(Br_2)$ requires Br (total), 54·9; Br (labile), 36·6 per cent.].

sym-p-*Chlorophenylethylthiocarbamide*.—A hot solution of *p*-chlorophenylthiocarbimide (10 g.) in alcohol (50 c.c.) was treated with 10 c.c. of a 33% aqueous solution of ethylamine, and the mixture was boiled for one minute and then cooled. On re-crystallisation from dilute methyl alcohol, the thiocarbamide formed slender needles, m.p. 119°. (Found: Cl, 16·4; S, 14·9. $C_9H_{11}N_2ClS$ requires Cl, 16·6; S, 14·9 per cent.). Yield: 12 g.

5-Chloro-1-ethylaminobenzthiazole hydrotetrabromide was prepared by heating sym.-*p*-chlorophenylethylthiocarbamide (2 g.) in chloroform (15 c. c.) with bromine (8 c. c.) for 15 minutes; the solution was filtered hot and cooled in an evacuated desiccator, when the *hydrotetrabromide* crystallised in deep red prisms, m. p. 64-66° (softening at 58°). [Found: Br (total), 60·0; Br (labile), 46·0. $C_9H_9N_2ClS$, $HBr(Br_3)$ requires Br (total), 60·1; Br (labile) 45·1 per cent.]. *5-Chloro-1-ethylaminobenzthiazole* separated from methyl alcohol in prisms, m. p. 159°. (Found: Cl, 16·8; S, 15·3. $C_9H_9N_2ClS$ requires Cl, 16·7; S, 15·1 per cent.). *5-Chloro-3-bromo-1-ethylaminobenzthiazole hydrotribromide*, prepared by adding bromine (8 c.c. in 15 c.c. of chloroform) to a solution of the 5-chloro-1-ethylamino-base (2 g.) in chloroform (50 c.c.), formed microscopic yellow prisms, m. p. 181-83° (decomp. with charring). [Found: Br (total), 60·1; Br (labile), 31·0. $C_9H_8N_2ClBrS,HBr(Br_2)$ requires Br (total), 60·1; Br (labile), 30·1 per cent.].

5-Chloro-3-bromo-1-ethylaminobenzthiazole crystallised from ethyl alcohol in long, slender needles, m. p. 155°. (Found: Br, 27·1. $C_9H_8N_2ClBrS$ requires Br, 27·4 per cent.)

5-Chloro-3-bromo-1-ethylaminobenzthiazole dibromide formed yellow needles, m. p. 190°. [Found: Br (total), 58·7; Br (labile), 35·5. $C_9H_8N_2ClBrS(Br)$ requires Br (total), 58·2; Br (labile), 35·4 per cent.]

sym-p-*Chlorophenyl*-n-*propylthiocarbamide* crystallised in slender needles, m. p..110°. [Found: Cl, 15·4; S, 14·1. $C_{10}H_{13}N_2ClS$ requires Cl, 15·5; S, 14·0 per cent.)

5-*Chloro*-1-n-*propylaminobenzthiazole hydrotetrabromide*, prepared in the usual way, crystallised in small red prisms, m. p. 87°. (Found: Br, 58·5. $C_{10}H_{11}N_2ClS,HBr(Br_3)$ requires Br, 58·5 per cent.)

5-*Chloro*-1-n-*propylaminobenzthiazole* crystallised in prisms, m. p. 125°. (Found: Cl, 15·8; S, 14·3. $C_{10}H_{11}N_2ClS$ requires Cl, 15·7; S, 14·1 per cent.).

5-*Chloro*-3-*bromo*-1-n-*propylaminobenzthiazole hydrotribromide* formed small yellow prisms, m. p. 191° (sintering at 185°). (Found: Br, 58·7. $C_{10}H_{10}N_2ClBrS,HBr(Br_2)$ requires Br, 58·6 per cent.)

5-*Chloro*-3-*bromo*-1-n-*propylaminobenzthalzole* separated from ethyl acetate in needles, m.p. 190°. (Found: Br, 26·3. $C_{10}H_{10}N_2ClBrS$ requires Br, 26·2 per cent.).

5-*Chloro*-3-*bromo*-1-n-*propylaminobenzthiazole dibromide* formed yellow prisms, m. p. 173°. [Found: Br (total), 52·0; Br (labile), 33·8. $C_{10}H_{10}N_2ClBrS(Br_2)$ requires Br (total), 51·5; Br (labile), 34·4 per cent.]

sym-p-*Chlorophenyl*isobutylthiocarbamide crystallised from dilute methyl alcohol in small glistening plates, m.p. 122°. (Found: Cl, 14·4; S, 13·5. $C_{11}H_{15}N_2ClS$ requires Cl, 14·7; S, 13·2 per cent.).

5-*Chloro*-1-isobutylaminobenzthiazole *Hydrotribromide*.—The mixture obtained from sym-*p*-chlorophenylisobutylthiocarbamide (2 g. in 15 c.c. of chloroform) and bromine (2·6 c.c. in 1 c.c. of chloroform) was heated for 15 minutes and cooled in an evacuated desiccator after rapid filtration. The *hydrotribromide* crystallised in glistening orange-red plates, m.p. 101° (softening at 95-97°). [Found: Br (total), 49·7; Br (labile), 34·3. $C_{11}H_{13}N_2ClS,HBr(Br_2)$ requires Br (total), 49·8; Br (labile), 33·2 per cent.].

5-*Chloro*-1-isobutylaminobenzthiazole separated from methyl alcohol in needles, m.p. 138°. (Found: Cl, 15·1; S, 13·5. $C_{11}H_{13}N_2ClS$ requires Cl, 14·8; S, 13·3 per cent.). The bromination of this *iso*butylamino-base under the usual conditions gave rise to a *perbromide* having the composition required for a hydropentabromide of 5-chloro-3-bromo-1-*iso*butylaminobenzthiazole; m.p. 168°. (Found: Br, 66·8. $C_{11}H_{12}N_2ClBrS,HBr(Br_4)$ requires Br, 66·6 per cent.).

5-*Chloro*-3-*bromo*-1-isobutylaminobenzthiazole crystallised from methyl alcohol in white prisms, m.p. 93°. (Found: Br, 25·3. $C_{11}H_{12}N_2ClBrS$ requires Br, 25·0 per cent.).

5-Chloro-3-bromo-1-isobutylaminobenzthiazole dibromide formed glistening golden plates, m.p. 265° (softening at 195°). [Found: Br (total), 50·2; Br (labile), 32·9. $C_{11}H_{12}N_2ClBrS(Br_2)$ requires Br (total), 50·0; Br (labile), 33·4 per cent.].

Stability Experiments. (*i*) *Volumetric Method.*—A solution of the dibromide in chloroform was slowly hydrolysed by acetic acid containing a small quantity of water. At definite intervals, quantities of 25 c.c. of the liquid were withdrawn, run into 25 c.c. of *N*/10-silver nitrate, the liquid diluted to 150 c.c., and titrated with standard ammonium thiocyanate after acidification with nitric acid. Some difficulty was experienced in connexion with the end point, owing to the colour of the bromide solution. In later experiments, the chloroform was extracted with water and the Br′ ion estimated by the Fischer-Volhard method. This method also failed, owing to the action of the hypobromous acid on the indicator, and the low solubility of the bromides which necessitated the estimation of small concentrations of Br′ ion in a large volume of liquid.

(*ii*) *Gravimetric Method.*—A solution of exactly 0·0025 g. of the dibromide in 150 c.c. of dry chloroform was maintained at 29·5° in a thermostat and 25 c.c. of acetic acid containing 1 per cent. of water, were added. At given intervals of time, 50 c.c. of the liquid were withdrawn by means of a pipette, thrice extracted with 200 c.c. of water and the united extracts were treated with 5 c.c. of sulphurous acid to destroy hypobromous acid present. The solution obtained in this way was then acidified with nitric acid and the Br′ ion estimated gravimetrically in the usual way.

The method was unsuccessful, due to the process of extraction with water which carried the hydrolysis to completion. Several reagents were therefore investigated from the point of view of removing unchanged benzthiazole dibromide without liberation of hydrogen bromide (ethylene, amyl alcohol, etc.), but they were found to give products which were appreciably hydrolysed under the experimental conditions.

(*iii*) *Colorimetric Method.*—It was observed that solutions of the dibromides are usually orange in colour when freshly prepared, but become paler in intensity during hydrolysis. The hydrolysis experiments with acetic acid containing 1 per cent. of water at 29·5° described in the previous section, were therefore repeated, the hydrolysing solution being removed at definite intervals and examined by means of a simple type of nephelometer, consisting of two graduated tubes

illuminated by blue light. One cylinder containing the standard solution was compared with the other tube containing a given volume of the reaction mixture which had been kept at the standard temperature in the thermostat ; the observations being made by adjustment of the height of the standard column. Unfortunately, it was found that a small amount of red colouring matter was produced (by oxidation) during the hydrolysis of the dibromides, which masked the discharge of colour of the bromo-addition compound. The nature of these red coloured oxidation products has not yet been established but they are readily obtained by prolonged boiling of alcoholic solutions of the dibromides.

(*iv*) *Conductivity Method.*—During the hydrolysis of the dibromides, Br' ion is produced, and the course of the reaction should therefore be capable of being studied by observations on the change of electrical conductivity of the reaction mixture. The technique of the hydrolysis experiments in this case was the same as that employed in the previous experiments ; portions of the reaction mixture being removed at definite intervals of time and examined in a conductivity cell. Actually, however, our experiments showed that the change in conductivity was so small that it could not be determined with any accuracy with the apparatus at our disposal, and furthermore, the platinum electrodes of the conductivity cell become coated with a yellow deposit, which interfered with the investigation.

(*v*) *Dissociation Method.*—The details of this method and the general experimental technique have already been described by Ephraim (*loc. cit.*). We found it convenient to replace the large sulphuric acid bath by means of an electrical resistance furnace, using a platinum thermometer to surround the bulbs ; the thermometer being calibrated before each determination. In the cases of the ethylamino- and the *iso*butylamino-benzthiazole dibromides, which were the particular compounds studied in this connexion, thermal dissociation was inappreciable until within about 20° of the melting point of the compounds, when bromine was rapidly and continuously evolved, without any indication of a possible equilibrium of the type which we had anticipated.

The Bromination of the sym-*o*-*Tolylalkylthiocarbamides and the Hydroperbromides of the* 1-*Alkylamino*-3-*methylbenzthiazoles.*

The bromination of sym-*o*-tolylmethyl-, and sym-*o*-tolyl-*n*-propyl-thiocarbamides has already been described ; both of these thiocarba-

mides yield unstable hydrotetrabromides of the corresponding 1-alkylamino-3-methylbenzthiazoles (14).

sym-o-*Tolylethylthiocarbamide*.—A solution of *o*-tolylthiocarbimide in alcohol was treated with 20 per cent. excess of ethylamine, the solution was then boiled for a minute or two, cooled, and concentrated under reduced pressure at laboratory temperature. On recrystallisation from absolute alcohol, the thiocarbamide formed colourless prisms, m.p. 90°. (Found: S, 16·7. $C_{10}H_{14}N_2S$ requires S, 16·5 per cent.).

Bromination.—A suspension of the ethylthiocarbamide (2 g.) in chloroform (12 c.c.) was treated with bromine (2 c.c. in 3 c.c. of the same solvent) and the mixture was heated under reflux for 10 minutes, cooled, and concentrated in a vacuum, when the *hydrotetrabromide* of 1-ethylamino-3-methylbenzthiazole separated in small orange-yellow prisms, which were rapidly dried in a vacuum before analysis, m.p. 78° (effervescence at 140°). (Found: Br, 62·1. $C_{10}H_{12}N_2S$, $HBr(Br_3)$ requires Br, 62·5 per cent.).

1-*Ethylamino*-3-*methylbenzthiazole* was obtained by suspending the hydrotetrabromide in sulphurous acid and treating it with sulphur dioxide until all solid matter was quite colourless ; the mixture being basified with ammonia (*d* 0·880). The base crystallised from ethyl acetate in white needles, m.p. 114°. (Found: S, 16·5. $C_{10}H_{12}N_2S$ requires S, 16·7 per cent).

sym-o-*Tolyl*-n-*butylthiocarbamide*, crystallised on keeping in an evacuated desiccator, and separated from alcohol in prisms, m.p. 53°. (Found: S, 14·1. $C_{12}H_{18}N_2S$ requires S, 14·4 per cent.).

Bromination.—A solution of the *n*-butylthiocarbamide (2 g.) in chloroform (10 c.c.) was treated with bromine (2 c.c.) as in the case of the ethyl compound. Concentration of the solution under reduced pressure yielded a highly unstable substance, having the composition required by that of a *hydrohexabromide* of 1-*n*-butylamino-3-methylbenzthiazole, which crystallised in small red needles, m. p. 61° (sintering at 55°), which were very rapidly dried on porous earthenware in vacuum, and *immediately* analysed with all the precautions used by Dyson, Hunter, and Soyka (15) in connexion with the unstable hydropentabromide of 5:4′-dibromoanilinobenzthiazole. This red perbromide was so unstable that it commenced to decompose with loss of bromine within 10 minutes. (Found: Br, 68·0. $C_{12}H_{16}N_2SHBr(Br_5)$ requires Br, 68·6 per cent.).

1-n-*Butylamino*-3-*methylbenzthiazole*, obtained by concentrating a solution of the gum obtained reduction of the hydrohexabro-

mide, in dilute methyl alcohol under reduced pressure, at laboratory temperature, formed colourless prisms, m. p. 50° (Found: S, 14·2. $C_{12}H_{16}N_2S$ requires S, 14·5 per cent.).

sym-o-*Tolyl*iso*butylthiocarbamide* formed colourless prisms, m. p. 68°. (Found: S, 14·6 per cent.).

Bromination.—The unstable bromo-addition compound obtained from the *iso*butylthiocarbamide had the comosition of a *hydrohexamide* of the 1-*iso*butylaminobenzthiazole, and formed red prisms, m. p. 70-72° (sintering at 60°). (Found: Br, 67·8 per cent.).

1-iso*Butylamino*-3-*methylbenzthiazole* separated from dilute methyl alcohol in short needles, m. p. 58°. (Found: S, 14·7 per cent.).

sym-o-*Tolyl*-n-*amylthiocarbamide*, prepared from the tolylthiocarbimide and *n*-amylamine, formed large colourless prisms, m. p. 74°. (Found: S, 13·8. $C_{13}H_{20}N_2S$ requires S, 13·6 per cent.).

Bromination.—A solution of the *n*-amylthiocarbamide (2 g.) in chloroform (10 c.c.) was treated with bromine (2 c.c. in 3 c.c. of the same solvent); the *hydrohexabromide* formed silky orange-red needles, which rapidly decomposed leaving a yellow residue of a lower bromo-addition compound: m. p. 61° (sintering at 55°). (Found: Br, 66·4. $C_{13}H_{15}N_2SHBr(Br_5)$ requires Br, 67·2 per cent.).

1-n-*Amylamino*-3-*methylbenzthiazole* separated from dilute methyl alcohol in white prisms, m. p. 48°. (Found: S, 13·9. $C_{13}H_{18}N_2S$ requires S, 13·7 per cent.).

sym-o-*Tolyl*iso*amylthiocarbamide*, prepared from *iso*amylamine, formed small white prisms, m. p. 57°. (Found: S, 13·1 per cent.).

1-iso*Amylamino*-3-*methylbenzthiazole hydrohexabromide*, prepared as in the case of the *n*-amyl derivative from 2 g. of sym-o-tolyl-*iso*amylthiocarbamide, separated in glistening red needles, m. p. 57° (sintering at 50°). (Found: Br, 66·8 per cent.). This compound decomposed turning yellow with loss of bromine, on keeping for 10 minutes.

1-iso*Amylamino*-3-*methylbenzthiazole*.—The gum obtained by reduction of the hydrohexabromide, followed by basification with ammonia, crystallised with some difficulty from dilute methyl alcohol in small white crystals, m. p. 59°. (Found: S, 13·8 per cent.).

sym-o-*Tolyl*-n-*hexylthiocarbamide*, prepared by condensation of the tolylthiocarbimide with *n*-hexylamine, formed small white prisms, m. p. 76°. (Found: S, 13·2. $C_{14}H_{22}N_2S$ requires S, 12·8 per cent.).

1-n-*Hexylamino*-3-*methylbenzthiazole hydrohexabromide*, prepared from 2 g. of the hexylthiocarbamide, chloroform (13 c.c.), and bromine (2 c.c.), formed brilliant red needles, m.p. 58° (sintering

at 55°). (Found: Br, 65·2. $C_{14}H_{20}N_2S$, $HBr(Br_5)$ requires S, requires Br, 65·9 per cent.).

1-n-*Hexylamino-3-methylbenzthiazole* separated from dilute alcohol in long needles, m. p. 46°. (Found: S, 13·0. $C_{14}H_{20}N_2S$ requires S, 12·9 per cent.)

For the benefit of any future investigators, it may be statedhere that the 1-alkylamino-3-methylbenzthiazole field presents considerable experimental difficulty. Both the sym-*o*-tolylalkylthiocarbamides and 1-alkylamino-3-methylbenzthiazoles. from *n*-butyl onwards, form low melting solids which usually separate from their solutions in the form of tenacious gums, which frequently present considerable difficulty in recrystallisation. The hydroperbromides of the bases in addition to this, are most unstable and decompose under the ordinary conditions of drying in an evacuated desiccator. Indeed, concordant values for the analysis of these unstable bromo-addition compounds can only be obtained by careful and very rapid drying in a vacuum, followed by the immediate analysis. In the experiments just described the bromo-addition compounds were kept out of contact of the atmosphere until the actual moment of weighing.

The Methylation of 5-Fluoro-1-aminobenzthiazole and of 5-Iodo-1-aminobenzthiazole. (i) *Synthesis of 5-Fluoro-1-aminobenzthiazole from* p-*Fluoroaniline.*—(A) p-*Fluorophenylthiocarbimide.* Thiocarbonyl chloride (1 mol.) was completely suspended in cold water (10 vols.) by vigorous stirring during the addition of *p*-fluoroaniline (0·75 mol.), dissolved in chloroform (5 vols.). After half hour's stirring, the chloroform layer was removed and dried with calcium chloride and the solvent and excess of thiocarbonyl chloride were removed by evaporation on a steam-bath. The *fluorophenylthiocarbimide* obtained by fractionation of the residue, formed a refractive oil, b. p. 228°/760 mm. (Found: S, 21·3. C_7H_4NFS requires S, 20·9 per cent.). Yield: 70-80%. (B) p-*Fluorophenylthiocarbamide*, prepared by treating an alcoholic solution of the thiocarbimide with excess of ammonia (*d* 0·880) and warming the solution on a water-bath, crystallised from alcohol in glistening needles, m. p. 164°. (Found: S, 19·3. $C_7H_7N_2FS$ requires S, 18·9 per cent).(C) *Bromination.* *p*-Fluorophenylthiocarbamide (1 g.) in chloroform (10 c.c.) was treated with bromine (1 c.c. in 1 c.c. of chloroform) and the mixture was heated on a steam-bath for 10-15 minutes and cooled. The bromo-addition compound obtained in this way, was suspended in sulphur-

ous acid and treated with sulphur dioxide until reduction was complete. On basification and recrystallisation from alcohol, *5-fluoro-1-aminobenzthiazole* was obtained in small white plates, m. p. 182°. (Found: S, 18·8. $C_7H_5N_2FS$ requires S, 19·0 per cent.).

5-Fluoro-1-acetaminobenzthiazole obtained by heating a solution of the fluoro-base in acetic anhydride for a few minutes, diluting the solution with alcohol and concentrating the mixture on a steam-bath crystallised from alcohol-ethyl acetate in white plates, m. p. 221°. (Found: S, 15·6. $C_9H_7ON_2FS$ requires S, 15·3 per cent.).

Methylation of 5-Fluoro-1-aminobenzthiazole and the Synthesis of 5-Fluoro-1-methylaminobenzthiazole by way of sym-p-*Fluorophenylmethylthiocarbamide*.—(A)4 c.c. of methyl sulphate were added to a solution of 1 g. of 5-fluoro-1-aminobenzthiazole in alcohol (10 c.c.) and the solution was heated on a steam-bath under reflux; 2 g. of potassium hydroxide were then added. The mixture was diluted with 100 c.c. of water, kept for 30 minutes, and then extracted with chloroform. The gum obtained by removal of the chloroform could not be crystallised. It was therefore acetylated by treatment with excess of hot acetic anhydride, followed by dilution with alcohol; the solution being thereafter concentrated on a steam-bath. The product which consisted of *5-fluoro-1-acetimino-2-methyl-1:2-dihydrobenzthiazole* (m. p. 190°), had m. p. 197° after several recrystallisations from alcohol. (Found: S, 14·6. $C_{10}H_9ON_2FS$ requires S, 14·3 per cent.). A careful search of the mother-liquors failed to reveal the presence of the isomeric *5-fluoro-1-acetylmethylaminobenzthiazole*, which was rationally synthesised as described below.

(B). sym-p-*Fluorophenylmethylthiocarbamide* was prepared by adding excess of an aqueous solution of methylamine (33%) to a solution of the fluorophenylthiocarbimide in alcohol. It formed a conglomerate mass of brownish waxy needles, m. p. 70°. (Found: S, 17·2. $C_8H_9N_2FS$ requires S, 17·4 per cent.).

5-Fluoro-1-methylaminobenzthiazole.—The fluorophenylmethylthiocarbamide (0·5 g.) in chloroform (6 c.c.) was treated with bromine (0·4 c.c.) and the mixture was heated under reflux, and the bromo-addition compound was reduced with sulphurous acid. The methylamino-*base* crystallised from alcohol in white prisms, m.p. 174°. (Found: S, 17·6 per cent.). The *acetyl* derivative, prepared by acetylation with acetic anhydride, crystallised from alcohol—ethyl acetate in needles, m. p. 156°. (Found: S, 14·4. $C_{10}H_9ON_2FS$ requires S, 14·3 per cent.).

(*ii*) *Synthesis of 5-Iodo-1-aminobenzthiazole.*—5-Iodo-1-aminobenzthiazole was prepared by bromination of *p*-iodophenylthiocarbamide in chloroform under conditions similar to those used in connexion with the fluoro-derivative. It crystallised from alcohol in needles, m.p. 210°. (Found: S, 11·8. $C_7H_5N_2IS$ requires S, 11·6 per cent.).

Methylation.—A mixture of 5-iodo-1-aminobenzthiazole (1 g.), methyl sulphate (4 c.c.) and alcohol (10 c.c.) was heated on a steam-bath under reflux for 10 minutes. Solid potassium hydroxide (2 g.) was then added to the mixture, which was diluted with water and extracted with chloroform. Removal of the chloroform yielded a gum, which was dissolved in acetone and treated with a solution of 2 g. of picric acid in the same solvent, when the *picrate* of 5-iodo-1-imino 2-methyl-1:2-dihydrobenzthiazole separated (1·5 g.) in the form of short yellow prisms, which were fairly soluble in acetone, m. p. 222°. (Found: S, 6·4. $C_8H_7N_2IS$, $C_6H_3O_7N_3$ requires S, 6·3 per cent.). The presence of the picrate of the isomeric methylamino-base (m. p. 245°) could not be detected.

Synthesis of 5-Iodo-1-methylaminobenzthiazole.—sym-*p-Iodophenylmethylthiocarbamide*, prepared from *p*-iodophenylthiocarbimide and methylamine in alcohol, crystallised in needles, m.p. 169°. (Found: S, 11·3. $C_8H_9N_2IS$ requires S, 10·9 per cent.). *5-Iodo-1-methylaminobenzthiazole*, prepared by bromination of the iodophenylmethylthiocarbamide in chloroform, followed by reduction with sulphurous acid and basification with ammonia in the usual way, separated from alcohol in small white prisms, m.p. 219°. (Found: S, 11·2. $C_8H_7N_2IS$ requires S, 11·0 per cent.). The *acetyl* derivative, prepared by heating a solution of the methylamino-base in acetic anhydride for a few minutes, and diluting the resulting solution with alcohol, crystallised in white plates, m.p. 185°. (Found: S, 11·0. $C_{10}H_9ON_2IS$ requires S, 9·7 per cent). The *picrate*, prepared by mixing acetone solutions of the base and picric acid, crystallised in fine yellow needles which had m.p. 245°. (Found: S, 6·3. $C_8H_7N_2IS$, $C_6H_3O_7N_3$ requires S, 6·2 per cent.).

Thiazole Derivatives.

The Bromination of 2·4-Dimethylthiazole, the Formation of 5-Bromo-2 : 4-dimethylthiazole Hydropentabromide, and the Reduction of 5-Bromo-2:4-dimethylthiazole.—Thioacetamide was most conveniently prepared in a pure condition by heating a mixture of acetamide and phosphorus pentasulphide in benzene on a water-bath, under a reflux for 30-40 minutes; the thioamide being

obtained by crystallisation of the benzene mother-liquors ; glistening yellow plates, m.p. 107°. 2:4 Dimethylthiazole was prepared as follows: 12 G. of thioacetamide were gradually added to 18 c.c. of warm monochloroacetone in a large flask ; the mixture was gently heated on a wire gauze, extracted with 200 c.c. of hot 10% hydrochloric acid, and the extract was basified and extracted with ether. The ethereal solution of the thiazole was dried by means of anhydrous sodium sulphate, and the ether was distilled off from a water-bath, using an efficient fractionating column. The residual oil (12 g.), b.p. 135-145°, on redistillation yielded pure 2:4-dimethylthiazole as a highly refactive oil, possessing a strong pyridine-like odour, b.p. 143-144°/762 mm. The *chloroplatinate* of this base, prepared in the usual way from a solution of the thiazole in dilute hydrochloric acid and a 5 per cent. solution of platinum tetrachloride, crystallised in orange needles, m.p. 230-232° (decomp) on rapid heating. (Found : Pt, 31·0. Calc. Pt, 30·7 per cent.). Hantzsch recorded the m.p. of this compound as 215° (*Annalen*, 1889, **250**, 257).

5-Bromo-2:4-dimethylthiazole Hydropentabromide.—A solution of the dimethylthiazole (1·5 c.c., 2·5 g.) in chloroform (10 c.c.) was cooled to 0—2° and treated with 2 c.c. of bromine, when heat was evolved and the *hydropentabromide* crystallised on keeping the solution for a short time. This compound formed unstable, glistening red prisms which had m.p. 93-95° (decomp. with softening at 90°) after rapid drying on porous earthenware in a vaccum. [Found: Br (total), 78·4 ; Br (labile), 47·0. C_5H_6NBrS, $HBr(Br_4)$ requires Br (total), 80·9 ; Br (labile), 53·9 per cent.] The estimation of labile bromine was carried out in the usual way, by dissolving the bromo-addition compound in chloroform, to which a drop or two of acetic acid had been added, and adding a strong aqueous solution of potassium iodide ; the iodine liberated on shaking the mixture being titrated with $N/20$-sodium thiosulphate. In this estimation, a pink colouration was observed just before the end-point, which on addition of thiosulphate became pale yellow and finally colourless. It is highly probable that this accounts for the fact that the amoun t labile bromine is somewhat less than the calculated value for a hydropentabromide ; a small amount of the labile bromine in the compound, which is doubtless liberated as hypobromous acid, being absorbed in some oxidative reaction which produces a pink colouring matter. It may be noted that the amount of bromine used for the production of the hydropentabromide

in quite appreciably below that theoretically required, in the experiment just recorded. The same product was, however, also isolated in a similar experiment in which an excess of the halogen was employed.—1·5 c.c. of bromine was added to a solution of (0·6 c.c.) of the dimethylthiazole in chloroform (10 c.c.) at 0.° The hydropentabromide separated as a red oil, which crystallised after keeping at laboratory temperature for three days, forming red prisms which had m.p. 90-93°. (Found: Br (labile), 46·0 per cent.) The same compound was also prepared according to the following conditions.—A solution of the dimethylthiazole (1 g.) in chloroform (10 c.c.) was treated with bromine (1 c.c.) at 0° and the mixture was kept for 2 hours, when the hydropentabromide crystallised in large red prisms, m.p. 93-95°. [Found: Br (total), 79·0; Br (labile), 47·5 per cent.]

5-Bromo-2:4-dimethylthiazole.—The hydropentabromide was added to sulphurous acid (saturated with SO_2 at 15°), when immediate reduction took place, and the mixture was basified with ammonia (*d* 0·880) and extracted with ether. The ethereal extract was dried with sodium sulphate, filtered, and the ether was removed through a fractionating column, and the residual oil was distilled. The *5-bromothiazole* formed a colourless, refractive oil, possessing a strong pyridine-like order, b.p. 188-190°/745 mm. (Found: Br, 41·8. C_5H_6NBrS requires Br, 41·7 per cent.). *Reduction.* A mixture of the 5-bromothiazole, granulated tin, and concentrated hydrochloric acid was warmed under reflux on a steam-bath, until a vigorous reaction set in. The reaction mixture was cooled, diluted with water and made strongly alkaline with 30 per cent. sodium hydroxide. Extraction of this mixture by ether, followed by removal of the ether on a steam-bath, yielded 2:4-dimethylthiazole which was identified by its properties, and the properties and analysis of the chloroplatinate which was obtained from the oil in the usual way. (Found: Pt, 31·3 per cent.).

The Bromination of 2-p-*Toluidino-4-methylthiazole, the Formation of 5-Bromo-*2-p-*toluidino-4-methylthiazole Hydrotribromide, and the Synthesis of* 2-o-*Bromo-*p-*toluidino-4-methythiazole.* (*i*) *Synthesis of* 2-p-*Toluidino-4-methylthiazole from Monochloroacetone and* p-*Tolylthiocarbamide.*—A mixture of 5 g. of *p*-tolylthiocarbamide and 4 c.c. of monochloroacetone was gently heated in a Geissler flask until a sudden reaction occurred; the heating was continued for a minute or two longer and the product was extracted with

100 c.c. of hot 15 per cent. hydrochloric acid. The extract was basified with sodium hydroxide and the thiazole *base* (6 g.) was recrystallised from methyl alcohol (animal charocal), when it formed glistening needles, m.p. 127-28°. (Found: N, 13·9 ; S, 15·8. $C_{11}H_{12}N_2S$ requires N, 13·7 ; S, 15·7 per cent.). (*ii*) *Bromination.* A solution of 2-*p*-toluidino-4-methylthiazole (0·5 g.) in chloroform (7 c.c.) was cooled to 0° and treated with bromine (0·6 c.c.). The red solution obtained in this way, was concentrated under reduced pressure at laboratory temperature, when the *hydrotribromide* of 5-bromo-2-p-toluidino-4-methylthiazole crystallised in glistening orange-red prisms, which were collected on porous earthenware and dried in a vacuum, m.p. 128-129° (decomp. with effervescence). [Found: Br (total) , 61·3 ; Br (labile), 25·0. $C_{11}H_{11}N_2BrS$, HBr (Br_2) requires Br (total), 61·1 ; Br (labile), 30·6 per cent.]. The low figure for labile bromine obtained by iodometric titration, is attributed to the error introduced by oxidation, alluded to in connection with the hydropentabromide of 5-bromo-2:4-dimethylthiazole. *Reduction.* The hydrotribromide (4 g.) was added to an excess of sulphurous acid, and sulphur dioxide was passed through the mixture till the reaction was complete. Basification and crystallisation of the product from alcohol, yielded a dark coloured product, which on recrystallisation from methyl alcohol (charcoal), yielded *5-bromo-2-p-toluidino-4-methylbenzthiazole* in the form of glistening plates, m.p. 142-143°. (Found: Br, 28·5. $C_{11}H_{11}N_2BrS$ requires Br, 28·3 per cent.)· (*iii*) 2-o-*Bromo-p-toluidino-4-methylthiazole* was obtained by condensing *o*-bromo-*p*-tolylthiocarbamide with an excess of monochloroacetone, under conditions similar to those employed in the case of 2-*p*-toluidino-4-methylthiazole. Extraction of the condensation product with hydrochloric acid, followed by basification, yielded the *thiazole* as an oil which crystallised from methyl alcohol in needles, m.p. 84-85°. (Found: Br, 28·7. $C_{11}H_{11}N_2BrS$ requires Br, 28·3 per cent.) This compound was much more soluble than the isomeric 5-brom o 2-*p*-toluidino-derivative already described.

The Methylation of 2-p-*Toluidino-4-methylthiazole and the Synthesis of* 2-p-*Tolylmethylamino-4-methylthiazole and of* 2-p-*Tolylimino-3: 4-dimethyl-2: 3-dihydrothiazole.*—(*i*) A mixture of 2-*p*-toluidino-4-methylthiazole (2 g.) and methyl iodide (2 c.c.) was heated at 100° for ten hours, and the product was basified with warm 20 per cent. potassium hydroxide and extracted with chloroform. The basic product was dissolved in methyl alcohol and fractionally crystallised

under reduced pressure at laboratory temperature. It appeared to consist solely of 2-p-*tolylimino*-3: 4-*dimethyl*-2: 3-*dihydrothiazole*, which had m.p. 107° alone, and when mixed with the specimen synthesised from monochloroacetone and sym-*p*-tolylmethylthiocarbamide. The presence of the isomeric 2-*p*-tolylmethylamino-4-methylthiazole could not be detected. In a similar experiment in which the methylation product was not basified, the product consisted entirely of the *hydriodide* of 2-*p*-tolylimino-3: 4-dimethyl-2: 3-dihydrothiazole, which crystallised from alcohol in needles, m.p. 224-226°. (Found: I, 36·4. $C_{12}H_{14}N_2S$, HI requires I, 36·8 per cent.). (*ii*) A mixture of asym-*p*-tolylmethylthiocarbamide (3·2 g.) and monochloroacetone (2 c.c.) was heated until a violent reaction took place, and the product was extracted with hydrochloric acid. 2-p-*Tolylmethylamino*-4-*methylthiazole*, obtained by basification of the extracts, crystallised from methyl alcohol in glistening plates, m.p. 60°. (Found: S, 15·0. $C_{12}H_{14}N_2S$ requires S, 14·7 per cent.). The solubility of this compound in methyl alcohol is considerably greater than that of the isomeric tolyliminomethyldihydrothiazole. (*iii*) A mixture of sym-*p*-tolylmethylthiocarbamide (4 g.) and monochloroacetone (2 c.c.) was heated until condensation took place, the product was extracted with hydrochloric acid, and the extracts were basified. On recrystallisation from methyl alcohol, 2-p-*tolylimino*-3: 4-*dimethyl*-2: 3-*dihydrothiazole* was obtained in small crystals, m.p. 107-108°. (Found: S, 14·9. $C_{12}H_{12}N_2S$ requires S, 14·7 per cent.).

The authors wish to express their gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in the progress of these investigations, to the Trustees of the Dixon Fund of the University of London for grants which have helped to defray the cost of the materials, and to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant to one of them (E. R. S.).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
AND
THE MUSLIM UNIVERSITY, ALIGARH.

Received January 7, 1931.

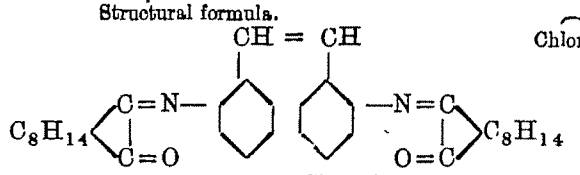
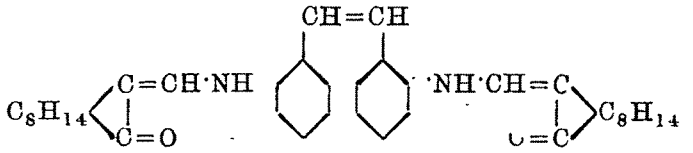
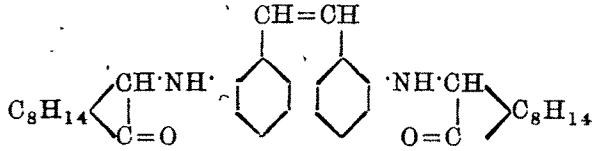
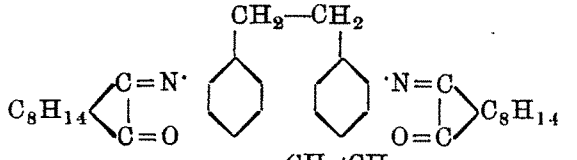
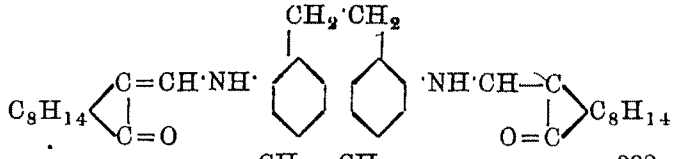
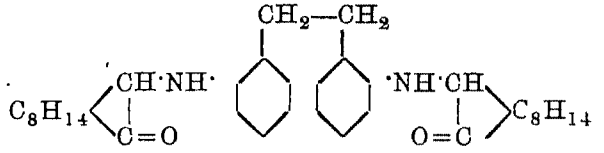
Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XI. The Rotatory Dispersion of Stereoisomeric *oo'*-Stilbene (*trans*) and *oo'*-Dibenzyl Derivatives of Bisimino-, Bisamino-, and Bisaminomethylene-camphors.

By Bawa Kartar Singh and Bhutnath Bhaduri.

The present communication is a continuation of Parts VIII and IX of this series and consists in the determination of the optical rotatory dispersion of the condensation products of oxymethylene camphors and camphorquinones with aromatic diamines, namely *oo'*-diaminostilbene and *oo'*-diaminodibenzyl. The measurements are made in six solvents as before.

The Effect of Conjugated Double Bonds and the Nature of the Solvent on Rotatory Power.—The remarkable effect of unsaturation and of conjugated linkages on optical activity has been noticed in previous publications (Forster and Thornley, *J. Chem. Soc.*, 1909, **95**, 942 ; Singh and collaborators, *ibid*, 1919, **115**, 566 ; 1920, **117**, 980, 1599 ; *J. Indian Chem. Soc.*, 1930, **7**, 545, 771). It is also brought out very clearly by comparing the structural formulæ depicted below, of the stilbene as well as the dibenzyl derivatives of bisiminocamphor, bisaminomethylenecamphor, and bisaminocamphor and their specific rotatory power in chloroform and pyridine (Table A). It is further seen that when the conjugation is broken at a distance from the asymmetric centre, the depression in the rotatory power is comparatively small (I⟶II and IV⟶V). but when the break in the conjugation occurs near that centre, there is considerable depression in the rotatory power (I⟶III ; IV⟶VI).

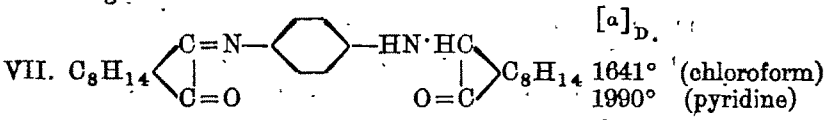
TABLE A.

Structural formula.	$[\alpha]^{35°}_{Hg_{green.}}$ Chloroform.	Pyridine.
I. 	456°	574°
II. 	394	435
III. 	45·6	149·8
IV. 	684	880
V. 	392	374
VI. 	157	122·6

Certain unexpected irregularities are however noticed in connection with the optical activity of two series of compounds derived from *oo'*-diaminostilbene and *oo'*-diaminodibenzyl. It was to be expected that the corresponding compounds derived from *oo'*-diaminostilbene (I, II, III) would show greater rotation than those derived from *oo'*-diaminodibenzyl (IV, V, VI). But it was found that *oo'*-stilbenebisiminocamphor (I) has lower rotation than *oo'*-dibenzylbisiminocamphor (IV) in all the solvents throughout the range of the spectrum investigated (compare Tables I—VI, IX—XIV ; also Fig. I). Again *oo'*-stilbenebisaminocamphor (III) has lower rotatory power than *oo'*-dibenzylbisaminocamphor (VI) in chloroform solution but higher, as was expected, in pyridine. It is thus clear that the nature

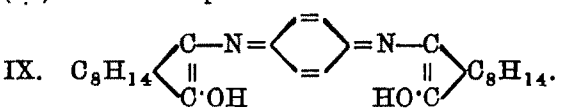
of the solvent can bring about this abnormal behaviour in rotatory power.

A similar irregularity has previously been observed by Forster and Saville (*J. Chem. Soc.*, 1921, **119**, 789) in connection with the rotatory power of camphorylaminophenyliminocamphor (VII) which was expected to be less than that of *p*-phenylenebisiminocamphor (VIII) but it is greater.

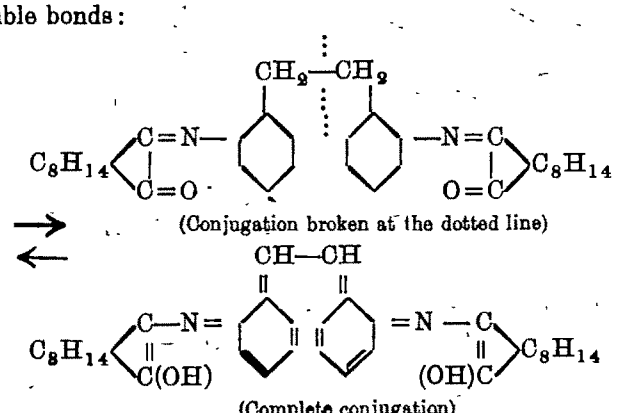


	$[\alpha]_D$.	
VII.	1641°	(chloroform)
	1990°	(pyridine)
VIII.	1508°	(chloroform)
	1528°	(pyridine)

The anomalous behaviour of camphorylaminophenyliminocamphor (VII) can however be explained by depicting the tautomeric formula (IX) for this compound.



The quinonoid arrangement postulated in this formula maintains an unbroken chain of conjugated double bonds and this explains its greater rotatory power. A similar explanation has already been advanced by us in the case of *pp'*-bisiminocamphordiphenylamine (*J. Chem. Soc.*, 1921, **119**, 1971) and *p*-iminocamphordiphenylamine (*J. Indian Chem. Soc.*, 1930, **7**, 545 ; *Trans. Faraday Soc.*, 1930, **27**, 347). It is likewise possible to bring in harmony the rotatory power of *oo'*-dibenzylbisiminocamphor with that of *oo'*-stilbenebisiminocamphor by postulating the following tautomeric arrangement for the former compound in which there is an unbroken chain of conjugated double bonds:



The Influence of Chemical Constitution and the Nature of Solvent on the Character of Rotatory Dispersion.—Oxymethylenecamphors and their condensation products with the aromatic diamines already described (*loc. cit.*) were found to obey the simple dispersion formula of Drude, $[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}$, where k is the "rotation" constant and λ_0^2, the "dispersion" constant of the equation. The compounds described in this paper, with one exception, also obey the same relation. The wide applicability of the simple dispersion formula to varied types or organic compounds is thus further established.

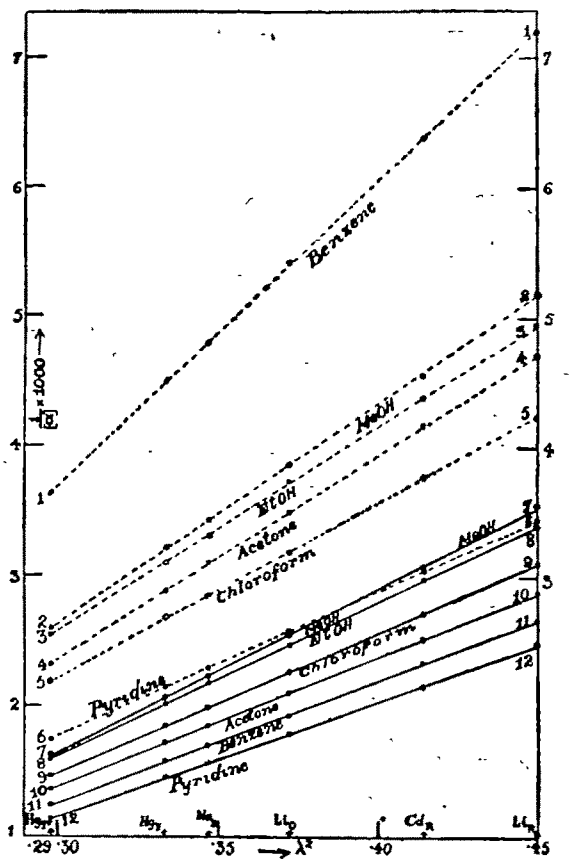


FIG 1.

Rotatory Dispersion of oo'-*Stilbenebisimino*-d-*camphor* (1—6) *and* oo'-*Dibenzylbisimino*-d-*camphor* (7—12).

The very exact straight lines of Figs. I and II which are obtained by plotting $1/[\alpha]$ against λ^2 show that the dispersion is simple with the exception of *oo'*-dibenzylbisaminocamphor which exhibits "*complex*" rotatory dispersion in pyridine (Curve 6, Fig. 2) and benzene and for which, dispersion equations with three constants have been worked out (Tables XIX and XX). It is rather strange tha the values of λ_o lie in the infra-red region. It is not however

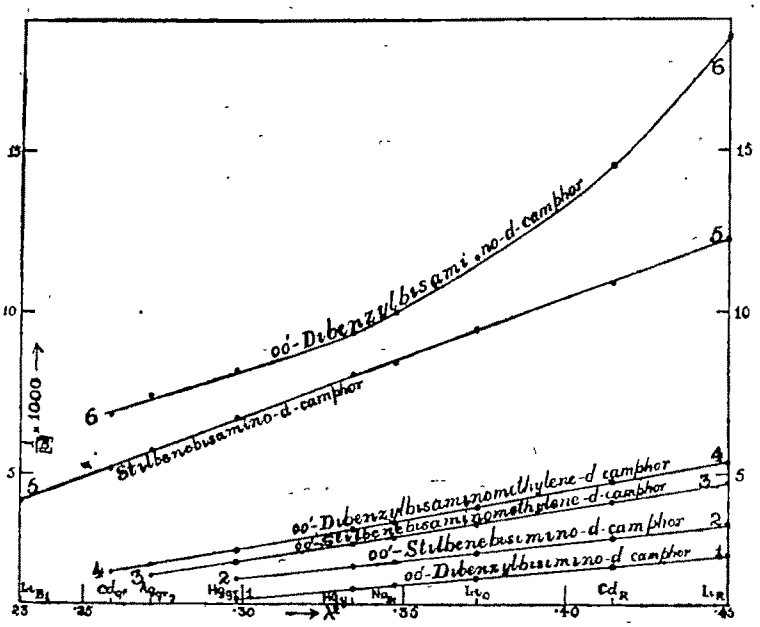


FIG 2.

Rotatory Dispersion in Pyridine ($t = 35°$).

possible to represent the rotatory dispersion of *oo'*-dibenzylbisaminocamphor in chloroform with a three constant equation (Table XXI). Fig. 2 also brings out graphically the influence of chemical constitution of these compounds on the rotatory dispersion in pyridine. A more exact test of the *simple* dispersion formula is given by numerical calculation. The tables of rotatory dispersion (Tables I—XVIII) show that the specific rotations, observed and calculated, of the enantiomeric *oo'*-stilbenebisiminocamphors, *oo'*-stilbenebisaminocamphors, *oo'*-dibenzylbisiminocamphors, *oo'*-stilbenebisaminocamphors and *oo'*-dibenzylbisaminomethylenecamphors, in different solvents lie well within the experimental error of 0·01° in the observed angle of rotation.

The value of λ_o, the wave-length of the hypothetical absorption band, usually in the ultraviolet region of the spectrum calculated from the dispersion formulae, may be correlated with the rotatory power of the compounds. An increase or decrease in the value of λ_o is accompanied by a corresponding increase or decrease in the specific rotation, as is seen in the following analysis: When the conjugation is broken by the reduction of the azethenoid groups as in the conversion of *oo'*-stilbenebisiminocamphors to *oo'*-stilbenebisaminocamphors the value of λ_o, in pyridine solution changes from 3787 to 3444 (A.U.) and the value of $[\alpha]_{Hg\ (green)}$ decreases from 574° to 150° (Tables V and VII). In chloroform solution the very considerable shift in the wave-length of the absorption band from 3689 to 1166 (A.U.) is accompanied by the phenomenal depression in the specific rotatory power from 456·8° to 45·6° for $Hg_{gr.}$ (Tables IV and VIII). The values of specific rotatory power and of λ_o are higher for *oo'*-dibenzylbisiminocamphor than for *oo'*-stilbenebisiminocamphor (Tables IX—XIV; I—VI). The same relationship between the values of λ_o and specific rotatory power is further exhibited by the remaining pair of compounds namely, *oo'*-stilbenebisaminomethylenecamphors and *oo'*-dibenzylbisaminomethylenecamphors (Tables XV, XVI; XVII, XVIII).

The Physical Identity of Enantiomers.—According to Pasteur's principle of molecular dissymmetry, enantiomorphic molecular configurations must possess the same total energy. They must show similar mechanical stability and therefore have an equal chance of being produced. They must also possess the same scalar properties; such as density, solubility, refraction, dispersion. But they must differ in those physical properties which are of directional (vectorial) nature, such as, for example, direction of rotation of the plane of polarisation of polarized light, unsymmetrical distribution of the hemihedral facets in their crystal forms, and also in the enantiomorphous distribution of pyro- and piezo-electrical polarity. On the other hand according to wave-mechanics (Temple, *Trans. Faraday Soc.*, 1930, **26**, 278) the *dextro* and *laevo* forms of a compound differ in energy and in rotatory power, although perhaps only to a very slight extent. The two views thus give different results. In support of the view derived from wave-mechanics, slight but distinct differences are alleged to exist in the rotatory power and other physical properties of *d*- and *l*-mandelic acids (Campbell and Garrow, *Trans. Faraday Soc.*, 1930, **26**, 560). But Pasteur's Law of Molecular Dissymmetry is too fundamental to be dismissed by an isolated

observation. It points to the necessity of making more observations on the equality or otherwise of the rotatory power of the *dextro*- and *laevo*-forms. The theoretical consequences emerging from such work are of fundamental importance. It is for this reason that we have made a comparative study of the rotatory power of the *dextro*- and *laevo*-isomerides of the compounds described in this and previous communications.

The individual readings of the angle of rotation did not differ from the mean by more than 0·02°. A calculation from the tables of rotatory dispersion will show that the maximum errors obtained by working out the effect on the result of the maximum deviation (0·02°) are well within the attainable limits of experimental accuracy. The maximum difference in the values of the observed specific rotatory power of the *dextro*- and *laevo*-forms of *oo'*-stilbenebisiminocamphor in acetone for Hg_{5780} (Table I), in chloroform for Na_{5893} (Table IV), and in pyridine for Li_{6104} (Table I), is 1·3°, whereas for a difference of 0·01° in the observed angle of rotation, the corresponding change in specific rotatory power is 2°. In the case of other compounds, these maximum observed differences are less than those calculated in the same way.

The inactive forms of *oo'*-stilbenebisiminocamphor, *oo'*-dibenzylbisiminocamphor and *oo'*-dibenzylbisaminomethylenecamphor melt at higher temperature than their optically active isomerides. These inactive forms are, therefore, true racemic compounds, at least in the solid state.

Experimental.

oo'-Stilbenebisimino-d-*camphor* (trans) (*Formula* I, Table A).

d Camphorquinone (1·66 g.) and (*trans*)-*oo'*-diaminostilbene (1·05 g.) were, in presence of fused sodium sulphate, heated at 140°—150° for 15-20 hours. The condensed product was extracted with acetone and crystallised as yellow prismatic needles melting at 231-32° (yield, 1·1 g.). It is easily soluble in chloroform, pyridine and benzene; less so in acetone and difficultly soluble in methyl alcohol, ethyl alcohol and ether. (Found: C, 80·51; H, 7·79; N, 5·86. $C_{34}H_{38}O_2N_2$ requires C, 80·63; H, 7·60; N, 5·53 per cent). The order of rotatory power in different solvents is as pyridine > chloroform > acetone > ethyl alcohol > methyl alcohol > benzene.

oo'-Stilbenebisimino-l-*camphor* was prepared in the same way as the corresponding *dextro*-isomer and has the same melting point,

solubility and rotatory power (Tables I—VI). (Found: N, 5·83. $C_{34}H_{38}O_2N_2$ requires N, 5·53 per cent.).

oo'- *Stilbenebisimino*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 238-39°. (Found: N, 5·76. $C_{34}H_{38}O_2N_2$ requires N, 5·53 per cent.).

oo'-*Stilbenebisamino*-d-*camphor* (*Formula* III, Table A).

oo'-Stilbenebisimino-*d*-camphor (1 g.) dissolved in benzene (75-80 c.c.) was shaken with zinc dust and caustic potash solution (12 %) for 20 hours, when it became colourless. The benzene layer was separated, washed with water and benzene distilled off; the residue was crystallised out of acetone as white prismatic needles (yield, 0·6 g.). It begins to decompose from 220°, melting completely at 240-41°. It is easily soluble in chloroform and pyridine; less so in acetone and benzene; and very difficultly in ethyl alcohol, methyl alcohol and ether. (Found: C, 79·86; H 8·30. $C_{34}H_{42}O_2N_2$ requires C, 80·00; H, 8·23 per cent.).

Rotatory power determinations were made only in two solvents *viz.*, pyridine and chloroform, as the compound is difficultly soluble in other solvents. Chloroform solution is slightly fluorescent, having a light blue colour in transmitted light.

oo'-*Stilbenebisamino*-l-*camphor* was prepared in the same way as the corresponding *dextro*-isomer and has the same melting point, solubility and rotation (Tables VII and VIII). (Found: N, 5·67. $C_{34}H_{42}O_2N_2$ requires N, 5·49 per cent.).

oo'-*Stilbenebisamino*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 210°-12° (faintly yellowish-white prismatic needles). (Found: N, 5·59. $C_{34}H_{42}O_2N_2$ requires N, 5·49 per cent.).

oo'-*Dibenzylbisimino*-d-*camphor* (*Formula* IV, Table A).

d-Camphorquinone (1·66 g.) and *oo'*-diaminodibenzyl hydrochloride (1·42 g.) were, in presence of fused sodium acetate, heated at 140-50° for 8 hours. The condensed product was extracted with alcohol, and crystallised as yellow prismatic needles melting at 187-88° (yield, 1·3 g.). It is readily soluble in chloroform, benzene and pyridine; less so in acetone; difficultly so in methyl alcohol, ethyl alcohol and ether. (Found: C, 80·18; H, 8·10. $C_{34}H_{40}O_2N_2$ requires C, 80·32; H, 7·87 per cent.).

The order of rotatory power in different solvents is as pyridine > benzene > acetone > chloroform > ethyl alcohol > methyl alcohol.

oo'-*Dibenzylbisimino*-l-*camphor* was prepared in the same way as the corresponding *dextro*-isomer and has the same melting point, solubility and rotatory power in different solvents (Tables IX-XIV). (Found: N, 5·54. $C_{34}H_{40}O_2N_2$ requires N, 5·51 per cent.).

oo'-*Dibenzylbisimino*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 194-95°. (Found: N, 5·72. $C_{34}H_{40}O_2N_2$ requires N. 5·51 per cent.).

oo'-*Dibenzylbisamino*-d-*camphor* (*Formula* VI, Table A).—oo'-Dibenzylbisimino-*d*-camphor (1·0 g.) dissolved in benzene was reduced in the usual way with 12% potassium hydroxide and zinc dust. Dry hydrochloric acid gas was passed through benzene solution when a black gummy solid separated. It was insoluble in water and turned brown. The suspended solid was neutralised with ammonium hydrate and the precipitate crystallised out of acetone as light cream coloured prismatic needles melting at 214-16° (yield, 0·45 g.). It is easily soluble in chloroform; less so in pyridine and benzene; difficultly soluble in acetone; sparingly soluble in methyl alcohol, ethyl alcohol and ether. (Found: C, 79·49; H, 8·88. $C_{34}H_{44}O_2N_2$ requires C, 79·69; H, 8·59 per cent.).

Rotatory power determinations were made only in three solvents *viz.*, chloroform, pyridine and benzene. as the compound is difficultly soluble in other solvents.

oo'-*Dibenzylbisamino*-l-*camphor* was prepared in the same way as the corresponding *dextro*-isomer and has the same melting point, solubility and rotatory power in different solvents (Table XIX-XXI). (Found: N, 5·65. $C_{34}H_{44}O_2N_2$ requires N, 5·47 per cent.).

oo'-*Dibenzylbisamino*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 204-05°. (Found: N, 5·64. $C_{34}H_{44}O_2N_2$ requires N, 5·47 per cent.).

oo'-*Stilbenebisaminomethylene*-d-*camphor* (*Formula* II, Table A). —*oo'*-Diaminostilbene (0·5 g.) in glacial acetic acid was added to a concentrated solution of oxymethylene-*d*-camphor (0·9 g.) in alcohol when a yellow precipitate separated at once. It was crystallised out of pyridine as shining light yellow prisms melting at 295-96° (yield,

0·9 g.). It is fairly soluble in chloroform; less so in pyridine; and sparingly soluble in methyl alcohol, ethyl alcohol, acetone, benzene, ether, and glacial acetic acid. (Found: C, 80·90; H, 8·22. $C_{36}H_{42}O_2N_2$ requires C, 80·91; H, 7·86 per cent.).

Rotatory power determinations were made only in two solvents *viz.*, chloroform and pyridine, the substance being very insoluble in other solvents.

oo′-*Stilbenebisaminomethylene*-l-*camphor* was prepared in the same way as the corresponding *dextro*-isomer and has the same melting point, solubility and rotation (Tables XV and XVI). (Found: N, 5·26. $C_{36}H_{42}O_2N_2$ requires N, 5·24 per cent.).

oo′-*Stilbenebisaminomethylene*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same melting point and similar solubility. (Found: N, 5·47. $C_{36}H_{42}O_2N_2$ requires N, 5·24 per cent.).

oo′-*Dibenzylbisaminomethylene*-d-*camphor* (*Formula* V, Table A). —oo′-Diaminodibenzyl (0·55 g.) in 50% acetic acid was added to a concentrated solution of oxymethylene-*d*-camphor (0·95 g.) in alcohol when an almost white precipitate separated at once. It was crystallised out of benzene as shining faintly yellowish-white prisms melting at 266-68° (yield 0·8 g.). It is fairly soluble in chloroform; less soluble in pyridine and sparingly soluble in benzene, methyl alcohol, ethyl alcohol, acetone and ether. (Found: C, 80·50; H, 8·40; N, 5·28. $C_{36}H_{44}O_2N_2$ requires C, 80·60; H, 8·21; N, 5·23 per cent.).

Rotatory power determinations were made only in two solvents *viz.*, chloroform and pyridine, the compound being insoluble in other solvents.

oo′-*Dibenzylbisaminomethylene*-l-*camphor* was prepared in the same way as the corresponding *dextro*-isomer and has the same melting point, solubility and rotatory power (Tables XVII and XVIII). (Found: N, 5·30. $C_{36}H_{44}O_2N_2$ requires N, 5·23 per cent.).

oo′-*Dibenzylbisaminomethylene*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 272-73°. (Found: N, 5·30. $C_{36}H_{44}O_2N_2$ requires N, 5·23 per cent.).

The rotatory power determinations were made in a 2 dcm. jacketed tube at 35°. The value of λ_0, calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm,

TABLE I.

oo′-Stilbenebisiminocamphor in Acetone.

$$[\alpha] = \frac{68{\cdot}68}{\lambda^2 - 0{\cdot}1502} \; ; \; \lambda_o = 0{\cdot}3876.$$

Dextro					*Laevo*		
Concentration: g/100 c.c.	Obs.[α] =o.	o—c.	Line.	Calc. [α] =c.	o′—c.	Obs.[α] =o′.	Concentration: g/100 c.c.
0·2496	430·6°	+0·4°	Hg_{5461}	±430·2°	±0°	−430·6°	0·2520
,,	346·5	+0·4	Hg_{5780}	346·1	−0·9	345·2	,,
,,	322·5	−0·4	Na_{5893}	322·9	+0·5	323·4	,,
,,	286·4	+0·1	Li_{6104}	286·3	−0·5	285·8	,,
,,	240·4	−0·4	Cd_{6438}	240·8	−0·7	240·1	,,
,,	212·3	±0	Li_{6708}	212·3	±0	212·3	,,

TABLE II.

oo′-Stilbenebisiminocamphor in Methyl Alcohol.

$$[\alpha] = \pm\frac{58{\cdot}61}{\lambda^2 - 0{\cdot}1458} \; ; \; \lambda_o = 0{\cdot}3818.$$

Dextro					*Laevo*		
Concentration: g/100 c.c.	Obs.[α] =o.	o—c.	Line.	Calc.[α] =c.	o—c.	Obs.[α] =o′.	Concentration: g/100 c.c.
0·1272	385·2°	+0·4°	Hg_{5461}	±384·8°	−1·4°	−383·4°	0·1252
,,	310·7	−0·6	Hg_{5780}	311·3	+0·3	311·6	,,
,,	290·9	±0	Na_{5893}	290·9	+0·7	291·6	,,
,,	259·4	+1·0	Li_{6104}	258·4	+1·2	259·6	,,
,,	220·2	+2·4	Cd_{6438}	217·8	+1·9	219·7	,,
,,	192·7	±0	Li_{6708}	192·7	−1·0	191·7	,,

The compound was sparingly soluble in methyl alcohol; hence half the usual concentration was employed.

TABLE III.

oo′-Stilbenebisiminocamphor in Benzene.

$$[\alpha] = \pm\frac{42{\cdot}06}{\lambda^2 - 0{\cdot}1456} \; ; \; \lambda_o = 0{\cdot}3816.$$

Dextro					*Laevo*		
Concentration: g/100 c.c.	Obs.[α] =o.	o—c.	Line.	Calc.[α] =c.	o′—c.	Obs.[α] =o′.	Concentration: g/100 c.c.
0·2520	275·8°	+0·3°	Hg_{5461}	±275·5°	+0·5°	−276·0°	0·2500
,,	222·2	−0·9	Hg_{5780}	223·1	−1·1	222·0	,,
,,	208·4	±0	Na_{5893}	208·4	−0·4	208·0	,,
,,	184·5	−0·7	Li_{6104}	185·2	+0·8	186·0	,,
,,	156·8	+0·4	Cd_{6438}	156·4	−0·4	156·0	,,
,,	138·9	+0·8	Li_{6708}	138·1	−0·1	138·0	,,

TABLE IV.

oo′-Stilbenebisiminocamphor in Chloroform.

$$[\alpha] = \pm \frac{74{\cdot}04}{\lambda^2 - 0{\cdot}1361} \; ; \; \lambda_0 = 0{\cdot}3689.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs. [α] = o.	o—c.	Line.	Calc.[α] = c.	o′—c.	Obs. [α] = o′.	Concentration : g/100 c.c.
0·2520	456·3°	−0·4°	Hg_{5461}	±456·7°	−0·7°	−456·0°	0·2500
,,	378·1	−0.9	Hg_{5780}	374·0	±0	374·0	,,
,,	351·3	+0·8	Na_{5893}	350·5	−0·5	350·0	,,
,,	313·5	+0·4	Li_{6104}	313·1	+0·9	314·0	,,
,,	265·9	−0·2	Cd_{6438}	266·1	−0·1	266·0	,,
,,	236·1	+0·3	Li_{6709}	235·8	+0·2	236·0	,,

TABLE V.

oo′-Stilbenebisiminocamphor in Pyridine.

$$[\alpha] = \pm \frac{88{\cdot}90}{\lambda^2 - 0{\cdot}1434} \; ; \; \lambda_0 = 0{\cdot}3787.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] = o.	o—c.	Line.	Calc. [α] = c.	o′—c.	Obs.[α] = o′.	Concentration : g/100 c.c.
0·2512	574·1°	±0°	Hg_{5461}	±574·1°	−0·7°	−573·4°	0·2520
,,	465·8	−0·3	Hg_{5780}	466·1	+0·2	466·3	,,
,,	436·0	±0	Na_{5893}	436·0	+0·5	436·5	,,
,,	388·2	+0·4	Li_{6104}	387·8	−0·9	386·9	,,
,,	328·5	+0·7	Cd_{6438}	327·8	−0·4	327·4	,,
,,	290·7	+0·8	Li_{6708}	289·9	−0·2	289·7	,,

TABLE VI.

oo′-Stilbenebisiminocamphor in Ethyl Alcohol.

$$[\alpha] = \pm \frac{62{\cdot}37}{\lambda^2 - 0{\cdot}1869} \; ; \; \lambda_0 = 0{\cdot}3700.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] = o.	o—c.	Line.	Calc.[α] = c.	o—c.	Obs.[α] = o.	Concentration : g/100 c.c
0·2500	392·0°	−0·9°	Hg_{5461}	±392·9°	±0	−392·9°	0·2520
,,	322·0	+0·6	Hg_{5780}	321·4	±0	321·4	,,
,,	302·0	+0·8	Na_{5893}	301·2	+0·2	301·4	,,
,,	268·0	−0·8	Li_{6104}	268·8	−0·9	267·9	,,
,,	228·0	−0·3	Cd_{6438}	228·3	−0·1	228·2	,,
,,	202·0	−0·4	Li_{6708}	202·4	±0	202·4	,,

TABLE VII.

oo′-Stilbenebisaminocamphor in Pyridine.

$$[\alpha] = \pm\frac{26\cdot93}{\lambda^2 - 0\cdot1186}\ ; \quad \lambda_0 = 0\cdot3444.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′=c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·5008	239·6°	−1·2°	Cd_{4800}	±240·8°	−0·7	−240·1°	0·5050
,,	192·7	+0·4	Cd_{5086}	192·3	+0·4	192·7	,,
,,	175·7	−0·7	Ag_{5209}	176·4	−0·5	175·9	,,
,,	149·8	−0·2	Hg_{5461}	150·0	+0·2	150·2	,,
,,	124·8	−0·1	Hg_{5780}	124·9	−0·4	124·5	,,
,,	118·8	+1·1	Na_{5893}	117·7	−0·1	117·6	,,
,,	105·8	−0·1	Li_{6104}	106·0	−0·2	105·8	,,
,,	91·87	+0·86	Cd_{6438}	91·01	−0·11	90·9	,,
,,	81·81	+0·54	Li_{6708}	81·27	−0·26	81·01	,,

TABLE VIII.

oo′-Stilbenebisaminocamphor in Chloroform.

$$[\alpha] = \pm\frac{12\cdot94}{\lambda^2 - 0\cdot0136}\ ; \quad \lambda_0 = 0\cdot1166.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·5040	60·52°	+0·82°	Cd_{4880}	±59·70°	+1·4°	−61·0°	0·5000
,,	52·59	−0·22	Cd_{5086}	52·81	+0·19	53·0	,,
,,	49 61	−0·62	Ag_{5209}	50·23	−0·23	50·0	,,
,,	45·64	+0·16	Hg_{5461}	45·48	+0·52	46·0	,,
,,	40·68	+0·29	Hg_{5780}	40·39	+0·61	41·0	,,
,,	38·70	−0·10	Na_{5893}	38·80	+0·20	39·0	,,
,,	35·72	−0·34	Li_{6104}	36·06	−0 06	36·0	,,
,,	32·75	+0·47	Dd_{6438}	32·28	+0·72	33·0	,,
,,	29·76	+0·10	Li_{6708}	29·66	+0·34	30·0	,,

TABLE IX.

oo′-Dibenzylbisiminocampor in Benzene.

$$[\alpha] = \pm\frac{105\cdot3}{\lambda^2 - 0\cdot1684}\ ; \quad \lambda_0 = 0\cdot4104.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·4024	811·4°	−0·2°	Hg_{5461}	±811·6°	−0·4°	−811·2°	0·4032
,,	684·9	−0·8	Hg_{5780}	685·7	−0·6	685·1	,,
,,	590·2	+1·4	Na_{5893}	588·8	+1·5	590 3	,,
,,	516·9	+1·0	Li_{6104}	515 9	+1·2	517·1	,,
,,	427·4	−0·7	Cd_{6438}	428·1	−0·2	427·9	,,
,,	374·1	−0 3	Li_{6708}	374·4	+0·1	374·5	,,

TABLE X.

oo'-Dibenzylbisiminocamphor in Chloroform.

$$[\alpha] = \pm \frac{92 \cdot 72}{\lambda^2 - 0 \cdot 1625} \; ; \quad \lambda_0 = 0 \cdot 4031.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·4012°	684·1°	+0·7°	Hg_{5461}	±683·4°	+0·4°	−683·8°	0·4000
,,	539·6	−0·9	Hg_{5780}	540·5	+0·8	541·3	,,
,,	502·3	+0·5	Na_{5893}	501·8	−0·5	501·3	,,
,,	441·2	−0·2	Li_{6104}	441·4	+1·1	442·5	,,
,,	368·9	+0·9	Cd_{6438}	368·0	−0·5	367·5	,,
,,	321·6	−0·9	Li_{6708}	322·5	± 0	322·5	,,

TABLE XI.

oo'-Dibenzylbisiminocamphor in Pyridine.

$$[\alpha] = \pm \frac{112 \cdot 8}{\lambda^2 - 0 \cdot 1704} \; ; \quad \lambda_0 = 0 \cdot 4128.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =o′	o′−c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·4020	880·4°	−1·4°	Hg_{5461}	±881·8°	+0·2°	−882·0°	0·4048
,,	690·2	+1·3	Hg_{5780}	688·9	+0·4	689·3	,,
,,	638·0	+0·5	Na_{5893}	637·5	−0·1	637·4	,,
,,	557·2	−0·5	Li_{6104}	557·7	−0·5	557·2	,,
,,	462·7	+0·8	Cd_{6438}	461·9	+0·1	462·0	,,
,,	401·8	−1·5	Li_{6708}	403·3	−0·6	402·7	,,

TABLE XII.

oo'-Dibenzylbisiminocamphor in Ethyl Alcohol.

$$[\alpha] = \pm \frac{83 \cdot 99}{\lambda^2 - 0 \; 1642} \; ; \quad \lambda_0 = 0 \cdot 4052.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·2020	626·2°	−0·7°	Hg_{5461}	±626·9°	+0·6°	−627·5°	0·2000
,,	495·0	+0·7	Hg_{5780}	494·3	+0·7	495·0	,,
,,	458·0	−0·6	Na_{5893}	458·6	−1·1	457·5	,,
,,	403·4	+0·4	Li_{6104}	403·0	−0·5	402·5	,,
,,	335·4	−0·2	Cd_{6438}	335·6	−0·6	335·0	,,
,,	294·5	+0·5	Li_{6708}	294·0	+1·0	295·0	,,

TABLE XIII.

oo'-Dibenzylbisiminocamphor in Acetone.

$$[\alpha] = \pm\frac{99\cdot88}{\lambda^2-0\cdot1628}\ ;\quad \lambda_0 = 0\cdot4035.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concentration : g/100 c.c.
0·4056	788·4°	+0·9°	Hg_{5461}	±787·5°	±0·0°	−787·5°	0·4020
,,	581·9	−1·1	Hg_{5780}	583·0	−2·2	580·8	,,
,,	541·2	−0·2	Na_{5893}	541·4	−0·3	541·1	,,
,,	475·8	+0·3	Li_{6104}	476·1	−1·0	475·1	,,
,,	397·0	−0·2	Cd_{6438}	396·8	−1·3	395·5	,,
,,	347·7	± 0	Li_{6708}	347·7	−0·8	346·9	,,

TABLE XIV.

oo'-Dibenzylbisiminocamphor in Methyl Alcohol.

$$[\alpha] = \pm\frac{80\cdot26}{\lambda^2-0\cdot1680}\ ;\quad \lambda_0 = 0\cdot4099.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o°.	Concentration : g/100 c.c.
0·2916	615·2°	−1·0°	Hg_{5461}	±616·2°	−1·0°	−615·2°	0·2040
,,	483·7	+0·5	Hg_{5780}	483·2	−0·4	482·8	,,
,,	447·9	+0·3	Na_{5893}	447·6	+0·9	448·5	,,
,,	391·9	−0·3	Li_{6104}	392·2	−0·1	392·1	,,
,,	324·9	−0·7	Cd_{6438}	325·6	+0·4	326·0	,,
,,	285·2	+0·6	Li_{6708}	284·6	−0·3	284·3	,,

TABLE XV.

oo'-Stilbenebisaminomethylenecamphor in Chloroform.

$$[\alpha] = \pm\frac{57\cdot12}{\lambda^2-0\cdot1532}\ ;\quad \lambda_0 = 0\cdot3914.$$

Dextro					*Laevo*		
Concentration : g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concentration : g/100 c.c.
0·4048	541·2°	−0·4°	Cd_{5086}	±541·6°	+0·9°	−542·5°	0·4000
,,	483·1	−0·6	Ag_{5209}	483·7	+0·1	483·8	,,
,,	394·0	±0	Hg_{5461}	394·0	−0·2	393·8	,,
,,	316·2	+0·4	Hg_{5780}	315·8	−0·8	315·0	,,
,,	294·1	−0·1	Na_{5893}	294·2	+0·8	295·0	,,
,,	260·7	+0·3	Li_{6104}	260·4	−0·4	260·0	,,
,,	218·7	+0·1	Cd_{6438}	218·6	+0·2	218·8	,,
,,	191·4	−1·0	Li_{6708}	192·4	+0·1	192·5	,,

The solution did not exhibit mutarotation.

TABLE XVI.

oo'-Stilbenebisaminomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{63{\cdot}02}{\lambda^2 - 0{\cdot}153} \; ; \; \lambda_0 = 0{\cdot}3911.$$

Dextro					*Levo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α]. =c.	o′−c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·2056	530·3°	−2·4°	Ag_{5209}	±532·7°	+0·5°	−533·2°	0·2016
	435·4	+1·4	Hg_{5461}	434·0	−0·2	433·8	
	347.7	−0·3	Hg_{5780}	348·0	−0·8	347·2	
	325.9	+1·4	Na_{5893}	324·5	+0·4	324·9	
	287·0	±0	Li_{6104}	287·0	+0·7	287·7	
	240·7	−0·4	Cd_{6438}	241·1	−0·5	240·6	
	211·5	−0·6	Li_{6708}	212·1	+1·2	213·3	

The solution exhibited mutarotation ; $[\alpha]_{Hg_{5461}} = 435{\cdot}4°$ and $[\alpha]_{Hg_{5780}} = 347{\cdot}7°$ changing to 413·3° and 328·2° respectively in course of 15 hours. The change is accompanied with the deepening of the initial pale yellow colour.

Half the usual concentration was employed, the substance being difficultly soluble in pyridine.

TABLE XVII.

oo'-Dibenzylbisaminomethylenecamphor in Chloroform.

$$[\alpha] = \pm \frac{59{\cdot}78}{\lambda^2 - 0{\cdot}1455} \; ; \; \lambda_0 = 0{\cdot}3814.$$

Dextro					*Levo*		
Concentration : g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs.[α] =o′.	Concentration : g/100 c.c.
0·4040	527·2°	−0·9°	Cd_{5086}	±528·1°	+0·7°	−528·8°	0·4000
,,	475·2	−0·1	Ag_{5209}	475·3	+1·0	476·3	,,
,,	392·3	+0·8	Hg_{5461}	391·5	−0.2	391·3	,,
,,	316·8	−0·2	Hg_{5780}	317·0	−0·7	316·3	,,
,,	295·8	−0·5	Na_{5893}	296·3	±0	296 3	,,
,,	263·6	+0·4	Li_{6104}	263·2	−0·7	262·5	,,
,,	222·8	+0·6	Cd_{6438}	222·2	−0·9	221·3	,,
,,	195.5	−0·4	Li_{6708}	195·9	+0·4	196·3	,,

The solution does not exhibit any mutarotation.

TABLE XVIII.

oo′-Dibenzylbisaminomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{56{\cdot}59}{\lambda^2 - 0{\cdot}1472}; \quad \lambda_0 = 0{\cdot}3837.$$

Dextro						*Levo*		
Concentration: g/100 c.c.	Obs.[α] =o	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concentration: g/100 c.c.
0·2044	506·3°	−1·4°	Cd_{5086}	±507·7°	+1·2°	−508·9°	0·2024
,,	457·3	+1·2	Ag_{5369}	456·1	−1·7	454·4	,,
,,	374·2	−0·6	Hg_{5461}	374·8	+0·6	375·4	,,
,,	303·3	+0·5	Hg_{5780}	302·8	+1·0	303·8	,,
,,	283·7	+0·8	Na_{5893}	282·9	−1·3	281·6	,,
,,	251·9	+0·8	Li_{6104}	251·1	−1·6	249·5	,,
,,	210·3	−1·3	Cd_{6438}	211·7	+0·7	212·4	,,
,,	185·9	−1·0	Li_{6708}	186·9	−1·7	185·2	,,

TABLE XIX.

oo′-Dibenzylbisaminocamphor in Pyridine.

$$[\alpha] = \pm \frac{3{\cdot}28}{\lambda^2 - 0{\cdot}5390} \pm \frac{40{\cdot}73}{\lambda^2}; \quad \lambda_0 = 0{\cdot}7842.$$

Dextro						*Levo*	
Concentration: g/100 c.c.	Obs.[α] =o	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concentration: g/100 c.c.
0·2040	147·1°	+1·3°	Cd_{5086}	±145·8°	+1·7°	−147·5°	0·2000
,,	134·8	−3·0	Ag_{5369}	137·8	−2·8	135·0	,,
,,	122·6	−0·3	Hg_{5461}	122·9	−0·4	122·5	,,
,,	107·8	+1·9	Hg_{5780}	105·9	+1·6	107·5	,,
,,	100·5	+0·3	Na_{5893}	100·2	−0·2	100·0	,,
,,	85·83	−3·8	Li_{6104}	89·6	−4·6	85·0	,,
,,	68·63	−3·2	Cd_{6438}	71·8	−1·8	70·00	,,
,,	53·92	+0·2	Li_{6708}	53·7	+1·3	55·00	,,

Half the usual concentration was employed.

TABLE XX.

oo′-Dibenzylbisaminocamphor in Benzene.

$$[\alpha] = \pm \frac{35{\cdot}97}{\lambda^2 - 1{\cdot}424} \pm \frac{57{\cdot}12}{\lambda^2}; \quad \lambda_0 = 1{\cdot}1935.$$

Dextro						*Levo*	
Concentration: g/100 c.c.	Obs. [α] =o.	o−c.	Line	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concentration: g/100 c.c.
0·1992	190·7°	±0°	Cd_{5086}	±190·7°	+0·5°	−191·2°	0·2040
,,	178·2	−1·7	Ag_{5369}	179·9	−1·1	178·8	,,
,,	161·8	+1·5	Hg_{5461}	160·3	+2·7	163·0	,,
,,	138·0	−0·6	Hg_{5780}	138·6	−1·3	137·3	,,
,,	130·5	−1·2	Na_{5893}	131·7	−1·8	129·9	,,
,,	120·5	+0·8	Li_{6104}	119·7	+0·6	120·3	,,
,,	105·4	+2·7	Cd_{6438}	102·7	+2·7	105·4	,,
,,	90·36	−0·14	Li_{6708}	90·50	+0·17	90·67	,,

TABLE XXI.

oo'-Dibenzylbisaminocamphor in Chloroform.

Concentration : g/100 c.c.	Line.	Obs. [α] *Dextro* (*d*).	Obs.[α] *Leavo* (*l*).	Difference *d*−*l*.
0·3980 (*dextro*)	Cd_{4880}	+226·4°	−225·0°	+1·4°
0·4000 (*leavo*)	Cd_{5086}	187·2	187·5	−0·3
	Ag_{5209}	172·1	172·5	−0·4
	Hg_{5461}	157·0	157·5	−0·5
	Hg_{5780}	133·1	133·8	−0·7
	Na_{5893}	121·9	121·3	+0·6
	Li_{6104}	109·2	108·8	+0·4
	Cd_{6438}	99·24	98·8	+0·44
	Li_{6708}	81·66	81·3	+0·36

We wish to make grateful acknowledgment to the Government of Bihar and Orissa in the Ministry of Education, for the grant of a research scholarship to one of us (B. B.) which has enabled him to take part in this investigation.

We also wish to acknowledge the valuable assistance which we received from Babu Indramani Mahanti, B. Sc., the Head Assistant of the Chemical Department.

THE CHEMICAL LABORATORY,
RAVENSHAW COLLEGE, CUTTACK.

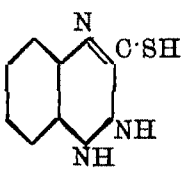
Received February 7, 1931.

Ring-Closure of o-Aminophenylsemicarbazides to Benzotriazines.

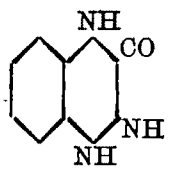
By P. C. Guha and F. Arndt.

(Experiments by Frl. Hedwig Skzypczik and P. S. Mayuranathan).

In a series of papers Guha and co-workers (*J. Indian Chem. Soc.*, 1925, **2**, 83 ; 1928, **5**, 439) have described reactions involving the ring-closure of carbonic acid derivatives of *o*-aminophenylhydrazine. To the products obtained by the action of *o*-aminophenylhydrazine upon potassium ethyl xanthogenate and carbamide, they ascribe the formulæ 3-mercapto-1:2-dihydro-1:2:4-benzotriazine (I) and 3-hydroxy-1:2-dihydro-1:2:4-benzotriazine (II) respectively.



(I)

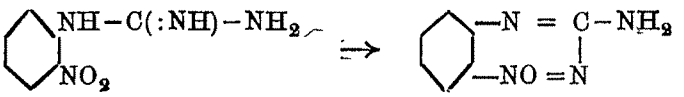


(II)

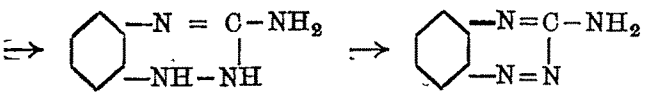
o-Nitrophenylsemicarbazide (III), *o*-nitrophenylthiosemicarbazide (IV) and methyl *o*-nitrophenyldithiocarbazinate (V) were obtained from *o*-nitrophenylhydrazine by the action of (*a*) cyanic acid, (*b*) thiocyanic acid and (*c*) carbon disulphide, alcoholic potash and methyl iodide. It was stated there that the reduction of the nitro to the amino group is accompanied by simultaneous splitting of water or hydrogen sulphide resulting in the formation of 3-amino-1:2-dihydro-1:2:4-benzotriazine (VI) from (III) and (IV) and 3-methylthiol-1:2-dihydro-1:2:4-benzotriazine (VII) from (V).

Arndt (*Ber.*, 1913, **46**, 3522) found that *o*-nitrophenylguanidine (VIII) by warming with alkali formed 3-amino-1-oxo-1:2:4-benzotriazine (IX) which passed on reduction to 3-amino-1:2-dihydro-1:2:4-benzotriazine (VI). This, however, could only be isolated as a

colourless nitrate: the free base suffered instantaneous oxidation to 3-amino-1:2:4-benzotriazine (X).



(VIII) (IX)



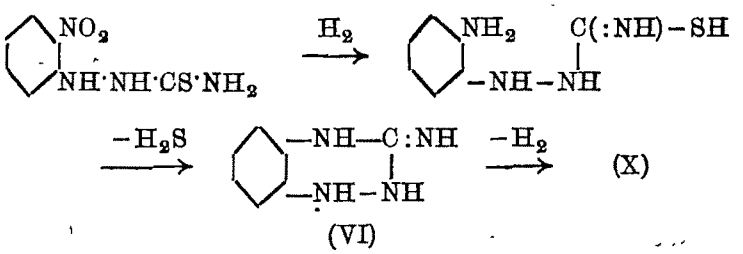
(VI) (X)

o-Nitrophenylcarbamide on similar treatment furnished in the end 3-hydroxy-1:2: 4-benzotriazine. From *o*-nitrophenylthiocarbamide Arndt and Rosenau (*Ber.*, 1917, **60**, 1248) obtained 3-mercapto-1-oxo-1:2:4-benzotriazine, the methylthiol derivative of which yielded on reduction a colourless salt solution of the dihydro-compound: the free base could not be isolated as it suffered immediate aerial oxidation to 3-methylthiol-1:2:4-benzotriazine. Later, Arndt (*Ber.*, 1927, **60**, 2598) obtained the same 3-methylthiol-1:2:4-benzotriazine by boiling the azo-compound $Ph-N:C(SCH_3)-N:N-CO-NH_2$ with organic solvents. A similar series of reactions were carried out also with the azo-body $Ph-N=C(NH_2)-N:N-C(SCH_3)=NH$ which by thermal decomposition gave directly the compound (X).

It appeared that the stability ascribed to the dihydrobenzotriazines by Guha and co-workers (*loc. cit.*) stood in direct contradiction to Arndt's work. With a view to explain this contradiction, by mutual agreement, the present work was undertaken simultaneously by both of us in our respective laboratories. The compounds (III) and (IV) were reduced exactly according to the method of Guha and the reaction mixture worked up when a base melting at 85° (*cf.* Guha who also gives 85°) was obtained which, however, on further careful purification melted at 101-102° and the substance was identified as such to be *o*-phenylenediamine and also in the form of its *p*-nitrobenzal derivative. Under the older experimental conditions the drastic reduction leads to a splitting between the two nitrogen atoms of the hydrazine group.

Now, the question before us was whether the reduction mechanism described by Guha could be realised under more suitable (*i.e.*, milder) conditions. Careful reduction of *o*-nitrophenylthiosemicarbazide (IV)

with a slight excess of stannous chloride and dilute hydrochloric acid, basification of the reaction mixture and repeated extraction with ether, furnished a colourless substance (transitory) which quickly changed to yellow. This substance is identical in all particulars with 3-aminobenzotriazine (X) (Arndt, *loc. cit.*) formed by rapid oxidation of the intermediate dihydro-derivative.



(VI)

Thus, the compound (X) is now obtained in a third way *viz.*, by ring-closure between positions 3 and 4 of the triazine ring ; while it was obtained by Arndt by ring-closure between positions 1 and 2 in one case and between 1 and 6 in another. It follows that the dihydrobenzotriazines possess the properties ascribed to them by Arndt and that they are not formed under Guha's older conditions of experiments.

Experimental.

The preparation of *o*-nitrophenylthiosemicarbazide and its reduction were carried out in the manner indicated previously by Guha (*loc. cit.*). The crystalline product obtained from alcohol and which melted according to Guha at 85°, gave after repeated crystallisation from ligroin and finally from alcohol, colourless crystals melting at 101-102°. This was identified as *o*-phenylenediamine by taking the mixed melting point with a genuine sample (Kahlbaum) as also by taking a mixed melting point of its *p*-nitrobenzal derivative (m.p. 138°) prepared from the diamine thus obtained and that prepared from a genuine sample.

Reduction under Milder Conditions: *Formation of* 3-*Amino*-1:2:4-*benzotriazine*.—*o*-Nitrophenylthiosemicarbazide (1 g.) was boiled under reflux with stannous chloride (4 g.) and 2*N*-hydrochloric acid (10 c.c.) till the solution ceased to give a blue colour with caustic alkali. The solution was made strongly alkaline with 2*N*-sodium hydroxide solution and thoroughly shaken with ether. The colourless ethereal layer soon became dark-yellow and began to deposit yellow needles

which dissolved on the further addition of ether. The ether extract was evaporated and the yellow residue recrystallised from alcohol, when yellow needles of aminobenzotriazine were obtained, m.p. 206°. Mixed melting point with a preparation obtained from *o*-nitrophenylguanidine gave no depression.

Both *o*-nitrophenylsemicarbazide and methyl *o*-nitrophenyldithiocarbazinate were prepared as stated by Guha (*loc. cit.*) and the products were in perfect agreement with those previously announced. On reduction according to Guha, the former gave *o*-phenylenediamine.

DEPARTMENT OF ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE, (INDIA).
AND
THE UNIVERSITY,
BRESLAU (GERMANY).

Received February 2, 1931.

Interaction of Sulphuryl Chloride with Substances containing the Reactive Methylene Group. Part II.

By K. G. Naik and N. T. Talati.

The present communication is a continuation of the work done by Naik and Shah (*J. Indian Chem. Soc.*, 1927, **4**, 11).

The main results of the interaction of sulphuryl chloride with various amides and substituted amides of malonic and methyl malonic acids, obtained herein, can be summarised as under:—

I. (*a*) Conversion of the group $:CH_2$ into $:CCl_2$ or (*b*) of the group :CHMe into :CClMe by complete replacement of the methylene hydrogen atom or atoms by chlorine, without chlorination of the nucleus:—Malon-di-*m*-nitranilide, malon-di-*p*-nitranilide, malon-di-*o*-nitranilide, malon-diethylamide, malon-di-*iso*butylamide, malon-diheptylamide, malon-di-1:4:5-xylidide, and malonamide undergo this change under (*a*) whereas methylmalon-diethylamide, methylmalon-di-*iso*butylamide, and methylmalon-dibenzylamide undergo this change under (*b*).

Further it was found that the same type of reactivity persisted even among the aliphatic amides of the methylmalonic acid. It may be noted here that in these compounds, one of the hydrogen atoms of the methylene group is replaced by the methyl group. Thus methylmalon-diethylamide, on interaction with sulphuryl chloride, yields a monochloro-derivative:—

$$(EtNH\cdot CO)_2\ CH\cdot Me + SO_2Cl_2 = (EtNH\cdot CO)_2\ CCl\cdot Me + HCl + SO_2$$

II. Conversion of the group $:CH_2$ into :CHCl without chlorination of the nucleus:—Malon-tetraphenylamide undergoes this change.

Type I. Malon-di-*m*-nitranilide reacts with sulphuryl chloride as under:—

$$(NO_2\cdot C_6H_4\cdot NH\cdot CO)_2CH_2 + 2SO_2Cl_2 = (NO_2\cdot C_6H_4\cdot NH\cdot CO)_2CCl_2 + 2HCl + 2SO_2.$$

The fact that the substance produced from malon-di-*m*-nitranilide has this constitution, is based on arguments similar to those advanced by Naik and Shah (*loc. cit.*).

It may, however, be pointed out that malontetraphenylamide, where there is no hydrogen atom attached to the nitrogen, yields a

monochloro-derivative. These go to prove that sulphuryl chloride reacts at the methylene group.

Type II. The interaction of malontetraphenylamide with sulphuryl chloride as stated above follows a different course, yielding a monochloro-compound:—

$$[Ph_2N{\cdot}CO]_2CH_2 + SO_2Cl_2 = [Ph_2N{\cdot}CO]_2CHCl + HCl + SO_2.$$

In this case, inspite of the two hydrogen atoms of the methylene group being available, only one is attacked. This course of the reaction is not an abnormal one, as is evident from the work of Naik (*J. Chem. Soc.*, 1921, **119**, 381), Naik and Shah (*loc. cit.*) and West (*J. Chem. Soc.*, 1922, **121**, 2196).

The experiments described here afford clear evidence, with regard to the reactivity towards sulphuryl chloride of compounds containing the reactive methylene group, that it depends on the electronegative character of the adjoining groups. For example, sulphuryl chloride reacts more vigorously with malon-dinitranilide than with malonamide, while the reaction with ethyl malonate is the most vigorous, taking place at the ordinary temperature. So in a series like:—

(I) $CH_2(CO{\cdot}NH_2)_2$
(II) $CH_2(CO{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2)_2$
(III) $CH_2(CO_2Et)_2$

the reactivity which is less pronounced in (I) becomes more and more manifest with increasing negative character of the adjoining groups.

Experimental.

*Preparation of Malon-di-*m- *and* -p-*nitranilides.*—These amides were prepared by condensing ethyl malonate and the corresponding nitraniline in equimolecular proportions, on the basis of the preparation of malonamide by Whiteley (*J. Chem. Soc.*, 1903, **83**, 36). The solid obtained was extracted with alcohol and finally crystallised from acetic acid in granulated mass. The *m*-compound had m. p. 196°, whereas the *p*-compound—a faintly yellowish crystalline one—had m. p. 243°.

*Preparation of Malon-di-*o-*nitranilide.*—The reaction with ethyl malonate and *o*-nitraniline did not go even at 200°. Hence the amide was prepared from malonic acid and *o*-nitraniline using phosphorus oxychloride as a condensing agent as used by Backes, West and

Whiteley (*J. Chem. Soc.*, 1921, **119**, 871). The amide was extracted with benzene in which it is soluble. It was crystallised from alcohol as yellowish, glistening, feathery needles, m. p. 182°. All the three malon-nitranilides were soluble in alcohol, acetic acid, benzene and toluene; sparingly so in carbon tetrachloride, chloroform, nitrobenzene, ethyl acetate but insoluble in ether, carbon disulphide and light petroleum. [Found: N, 16·41 (*ortho*), 16·48 (*meta*), 16·18 (*para*). $C_{15}H_{12}N_4O_5$ requires N, 16·28 per cent.].

*Dichloromalon-di-*m*-nitranilide.*—Malon-di-*m*-nitranilide (1 g.) and sulphuryl chloride (1 g.) were made to react by the method followed in the preparation of dichloromalon-diphenylamide (Naik and Shah, *loc.cit.*). The product obtained was crystallised from alcohol in grey leaflets, m.p. 166°.

It is fairly soluble in alcohol, acetic acid, benzene, and toluene; fairly so in nitrobenzene, carbon tetrachloride and ethyl acetate, but almost insoluble in ether, carbon disulphide and light petroleum. (Found : Cl, 17·81. $C_{15}H_{10}O_6N_4Cl_2$ requires Cl, 17·19 per cent.).

*Dichloromalon-di-*p*-nitranilide.*—The abve compound was obtained as a yellow crystalline mass when malon-di-*p*-nitranilide (1 g.) was treated with sulphuryl chloride (1 g.) in the presence of 50 c. c. of benzene in the usual way. It was crystallised from alcohol in yellowish needles, m.p. 178°. It behaves in almost the same way with different organic solvents, as the previous one does. (Found : Cl, 17·35. $C_{15}H_{10}O_6N_4Cl_2$ requires Cl, 17·19 per cent.).

*Dichloromalon-di-*o*-nitranilide.*—It was prepared from malon-di-*o*-nitranilide (1 g.) and sulphuryl chloride (1 g.) in the presence of dry benzene in the usual way. The solid product was crystallised from alcohol in yellowish prisms, m.p. 152°. The solubility of this compound is of the same order as that of the previous ones. (Found: Cl, 17·61. $C_{15}H_{10}O_6N_4Cl_2$ requires Cl, 17·19 per cent.).

Dichloromalon-diethylamide.—On treating malon-diethylamide (1 g.) with sulphuryl chloride (1 g.) in the usual way, white mass was deposited on standing. The resulting product was crystallised from alcohol in the form of white needles, m.p. 131°. The product has a solubility of the same order as that of the compound above described. (Found : Cl, 31·30. $C_7H_{12}O_2N_2Cl_2$ requires Cl, 30·28 per cent.).

*Dichloromalon-di-*isobutylamide.*—This compound was prepared from malon-di-*iso*butylamide (1 g.) and sulphuryl chloride (1·4 g.) in

the same way as the preceding chloride. After the reaction was over, the product crystallised from water in the form of white needles, m.p. 84°. It is soluble in almost all organic solvents except light petroleum. (Found : Cl, 25·19. $C_{12}H_{20}O_2N_2Cl_2$ requires Cl, 25·09 per cent.).

Dichloromalon-diheptylamide.—Malon-diheptylamide (1 g.) and sulphuryl chloride (1 g.) were made to react in the usual way described. The mass on crystallisation from benzene gave colourless prismatic needles, m.p. 90°. It is found to be identical with the dichloromalon-diheptylamide prepared by Naik add Trivedi (*J. Indian Chem. Soc.*, 1930, 7, 246) by condensation of the amide with selenium tetrachloride.

Dichloromalon-di-(1 : 4 : 5) *xylidide.*—The above compound was obtained as a colourless crystalline mass, when malon-di-(1 : 4 : 5) xylidide (2 g.) and sulphuryl chloride (2 g.) were treated in the usual way. It was crystallised from alcohol in colourless needles, m.p. 170°. It is found to be identical with dichloromalon-di-(1 : 4 : 5) xylidide prepared by Naik and Trivedi (*loc. cit.*)

Dichloromalonamide.—As under the above conditions the malonamide was inactive, it was directly treated with sulphuryl chloride. The reaction started slowly on heating, with an evolution of sulphur dioxide and hydrogen chloride. When the reaction slackened after three hours, the liquid was diluted with acetic acid and filtered hot. The filtrate on standing gave colourless, shining needles. They were washed with dry petroleum and crystallised from glacial acetic acid, m. p. 203°. It is found to be identical with dichloromalonamide prepared by Zincke and Kegel (*Ber.*, 1890, 23, 245).

Monochloromalon-tetraphenylamide.—Malontetraphenylamide (1 g.) and sulphuryl chloride (0·5 g.) were made to react as usual. The filtrate on leaving overnight deposited colourless crystals, which were recrystallised from benzene, m. p. 204°. It is found to be identical with monochloromalontetraphenylamide prepared by West (*J. Chem. Soc.*, 1922, 121, 2200) by direct chlorination of the amide.

Preparation of Methylmalon-diethylamide.—The amide was prepared from methylmalonic ester and ethylamine by the method of Backes, West and Whitely (*loc. cit.*, p. 366) adopted for the preparation of malon-diethylamide. The mass was crystallised from benzene in colourless needles, m. p. 151°.

It is fairly soluble in almost all organic solvents and also in water, but insoluble in light potroleum. (Found : N, 16·53. $C_8H_{16}O_2N_2$ requires N, 16·28 per cent.).

Monochloromethylmalon-diethylamide.—This compound was prepared by treating methylmalon-diethylamide (1 g.) with sulphuryl chloride (1 g.) in the usual way. Colourless needles were obtained on standing for a day. It was crystallised from alcohol, m. p. 108°. Its solubility in different organic solvents closely resembles that of dichloromalon-diethylamide. (Found: Cl, 17·61. $C_8H_{15}O_2N_2Cl$ requires Cl, 17·15 per cent.)

*Preparation of Methylmalon-di-*iso*butylamide.*—This amide is prepared from methylmalonic ester (10 g.) and *iso*butylamine (9 g.) by the method adopted by Backes, West and Whiteley (*loc. cit*) for the preparation of malon-*n*-propylamide. The mass was removed from the tube by dissolving in benzene. This solution on concentration gave white mass, which when crystallised from alcohol gave colourless needles, m. p. 133°. Its solubility is of the same order as that of the preceding compound. (Found : N, 12·64. $C_{12}H_{24}O_2N_2$ requires N, 12·28 per cent.).

*Monochloromethylmalon-di-*iso*butylamide.*—Methylmalon-di-*iso*butylamide (1 g.) and sulphuryl chloride (1 g.) were made to react in the usual way. The liquid on standing overnight, gave white mass, which when crystallised from alcohol yielded colourless needles, m. p. 102°. It closely resembles the preceding compound, in its solubility. (Found : Cl, 13·79. $C_{12}H_{23}N_2O_2Cl$ requires Cl, 13·52 per cent.).

Monochloromethylmalon-dibenzylamide. — This compound was prepared from methylmalondibenzylamide (2 g.) and sulphuryl chloride (2 g.) in the usual way. The product, when crystallised from benzene, gave shining pearly plates, m. p. 159°. It is soluble in chloroform and other organic solvents, like the above enumerated compound but is insoluble in light petroleum, ether and water. (Found : Cl, 11·18. $C_{18}H_{19}O_2N_2Cl$ requires Cl, 10·74 per cent.).

The authors desire to express their gratitude to His Highness the Maharaja Gaekwar's Government for a grant by which the expenses incurred in this research were met.

CHEMISTRY DEPARTMENT,
THE COLLEGE, BARODA.

Received January 12, 1931.

Sugden's Parachors. Part V. Mercaptans.

By Balwant Singh and Ram Singh.

Liquids can be classified broadly into two groups, which are usually distinguished by the terms "normal" and "associated". The latter show a number of abnormalities in their physical properties, which are usually explained by the formation of aggregates of simple molecules to give an easily dissociated complex.

According to Sidgwick ("The Electronic Theory of Valency", *pp.* 134-154) in the case of associated liquids, there is a combination between the molecules through the formatibn of co-ordinate links.

Taking Richards and Carver's results for the surface tension of ethyl alcohol at 20° (*J. Amer. Chem. Soc.*, 1921, 43, 827), Jones (*J. Chem. Soc.*, 1928, *p.* 1197) calculated its parachor, which has been found to be 126·7, while the theoretical value is 132·2. There is a contraction of −5·5 units at 20° for the single molecule, or −11 units for the double. This result is consistent with the view that association of alcohol takes place by co-ordination through hydrogen and it is accomplished by a singlet link, *i.e.*, C_2H_5-OH...OH-C_2H_5. One such bond requires a contraction of 12·4 units; this would the dimeric form. Thus it mean, apparently that the ethyl alcohol at 20° is on the average in is possible to account for these large contractions on the assumption that association involves single electron linkings (Sugden, *J. Chem. Soc.*, 1927, *p.* 1173).

Sidgwick and Bayliss (*J. Chem. Soc.*, 1930, *p.* 2031) from study of the parachors of *ortho*-phenols, have shown that the co-ordination of a hydrogen atom to form the group $=O\rightarrow H-$ involves a decrease of 14·4 units in the parachor of the single molecule. If this decrease represents the effect of the conversion of $>O+H-$ into $>O\rightarrow H-$, it should occur also in associated hydroxylic compounds in general.

Sulphur belongs to the same group of elements in the Periodic Table as oxygen. Each has six valency electrons and hence they possess analogous chemical properties. Oxygen, when it is present in combination with hydrogen as a hydroxy group —O-H, brings about association in hydroxylic compounds. The present work was undertaken to ascertain if sulphur in combination with hydrogen as the sulphydryl group —S-H would behave in the same way.

The parachors of a number of mercaptans have been determined in the fused state. Associated liquids, such as alcohols, phenols, fatty acids, etc., give parachors 4 to 8 units lower than the calculated values (Sugden, *J. Chem. Soc.*, 1924, **125**, 37; Jones, *loc. cit.*, Hunten and Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 161; Bhatnagar and Singh, *J. Indian Chem. Soc.*, 1930, **7**, 666).

Experimental.

p-Chlorophenyl mercaptan, m. p. 50°, *p*-bromophenyl mercaptan, m. p. 75°, *p*-tolylmercaptan, m. p. 42·5°, *p*-methoxy-*m*-tolyl mercaptan, m. p. 39° were prepared for this investigation by the method of Stewart (*J. Chem. Soc.*, 1922, **121**, 2555).

The parachor is then calculated by the formula: $P = y^{\frac{1}{4}} M/D$, in which M is the molecular weight, y is the surface tension in dynes/cm.; D is the density of the liquid at a given temperature. Densities were determined with a U-shaped pyknometer (Sugden, *J. Chem. Soc.*, 1924, **125**, 1171) and the surface tensions by the method of maximum bubble pressure using the apparatus described by Bhatnagar and Singh (*J. Chim. phys.*, 1928, **25**, 21). The results are given in Table I.

Table I.

Substance.	Temp. (°C).	Density (g./c.c.).	Surface tension dynes/cm.)	Parachor observed $P_{obs.}$	Parachor calculated $P_{calc.}$
1. Ethyl mercaptan*	2·0	0·8582	23·63	159·6	160·4
	16·7	0·8428	21·62	159·0	
			Mean	159·3	
2. Phenyl mercaptan†	16·9	1·080	38·46	254·0	
	25·5	1·074	37·67	253·9	
	35·0	1·059	36·31	255·4	255·3
	58·0	1·037	33·58	255·7	
	76·4	1·015	31·39	256·8	
			Mean	255·2	

* Ethyl mercaptan (Ramsay and Shields, *J. Chem. Soc.*, 1893, **63**, 1089).

† Phenyl mercaptan (Morgan and Chazal, *J. Amer. Chem. Soc.*, 1913, **38**, 1821).

	Substance.	Temp. (°C).	Density (g./c.c.).	Surface tension (dynes/cm.)	Parachor observed $P_{obs.}$	Parachor calculated $P_{calc.}$
3.	*p*-Chlorophenyl mercaptan.	60·0	1·224	36·80	291·1	
		70·0	1·214	35·90	291·7	
		80·0	1·204	34·52	291·2	292·5
		100·0	1·186	32·36	290·9	
				Mean	291·2	
4.	*p*-Bromophenyl mercaptan.	82·5	1·526	36·51	304·5	
		100·0	1·512	35·34	304·8	306·2
		116·5	1·494	33·79	305·0	
				Mean	304·8	
5.	*p*-Tolyl mercaptan.	50·5	1·022	33·84	292·8	
		64·4	1·010	32·48	293·3	294·3
		80·1	1·001	31·65	294·1	
				Mean	293·4	
6.	*p*-Methoxy-*m*-tolyl mercaptan.	44·6	1·093	36·48	346·5	
		59·7	1·081	35·51	348·0	353·3
		75·5	1·067	34·10	349·1	
				Mean	347·9	
7	Benzyl mercaptan.	18·5	1·058	39·26	293·6	
		30·0	1·047	37·96	294·1	294·3
		41·2	1·038	36·84	294·5	
				Mean	294·1	

From the above results, it is evident that the parachors calculated are in good agreement with the observed parachors except in case of *p*-methoxy-*m*-tolyl mercaptan where the values differ by 5·4 units owing to the presence of a methoxy-group (Bhatnagar and Singh, *loc. cit.*). The mercaptans, therefore, are not associated in the liquid or in the fused state. They behave as normal liquids. This is supported by the work of Auwers (*Z. phys. Chem.*, 1893, 12, 689; *ibid.*, 1899, 30, 529). From the determination of the molecular weights of a large number of mercaptans, alcohols and phenols in benzene and napthalene by the cryoscopic method, he has shown that the mercaptans are cryoscopically normal substances as compared with the alcohols and the phenols. This fact is clearly borne out by the results given in Table II, where in the first five cases benzene is the solvent, while in the last two cases napthalene is the solvent.

TABLE II.

Substance.	Mol. weight.	Substance in 100 g. of solvent (g.).	Observed depression (°C).	Mol. weight (calc.).
1. Methyl alcohol	32	0·32	0·360	43
		0·66	0·612	53
		1·80	1·265	70
		4·42	1·978	110
		7·29	2·475	144
2. Benzyl alcohol	108	0·35	0·170	101
		0·74	0·310	106
		2·82	1·038	132
		5·12	1·510	165
3. Phenol	94	0·30	0·100	145
		1·27	0·410	152
		2·98	0·925	158
		3·93	1·175	164
4. β-Naphthol	144	0·38	0·135	187
		1·06	0·365	142
		2·32	0·740	154
5. Thiophenol	110	0·51	0·236	106
		1·01	0·458	110
		2·08	0·930	110
		4·30	1·928	109
6. p-Chlorothiophenol	144·5	1·10	0·541	140
		2·50	1·180	146
		4·98	2·350	146
		9·06	4·257	146
7. p-Methoxy thiophenol	140	0·82	0·402	141
		3·31	1·597	143
		5·72	2·665	148
		7·19	3·370	147

Molecular weights calculated as well as observed by the cryoscopic method in the case of the mercaptans are in fair agreement whilst the alcohols and the phenols give abnormal molecular weights in solution. Hence the presence of a sulphydryl group in mercaptans does not promote association.

The authors desire to thank Prof. S. S. Bhatnagar for advice and guidance.

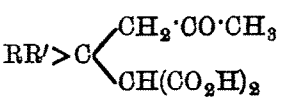
UNIVERSITY CHEMICAL LABORATORIES,
LAHORE AND KHALSA COLLEGE, AMRITSAR.

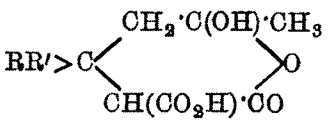
Received March 9, 1931.

On the Constitution of some δ-Ketodicarboxylic Acids.

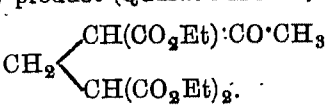
By Muhammad Qudrat-i-Khuda.

In a series of papers a systematic study of the properties of some δ-ketodiearboxylic acids has recently been described (Qudrat-i-Khuda, *J. Chem. Soc.*, 1929, pp. 201, 713, 1913). The results pointed towards the conclusion that the acids of the type (I) where both R and R′ are either alkyl groups or part of a ring system, exist at least under certain conditions in the lactol modification (II) also.

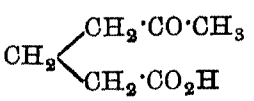




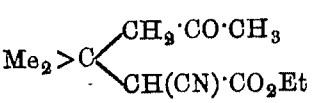
The effect of *gem*—substitution in promoting the ease of ring-formation is well known. It is, therefore, quite natural that the acids, such as (II) were found to be capable of existence. An extension of the experiments to acids in which either one or both of the substituting groups R and R′ are hydrogen atoms, is now under examination. In such acids the effect of the molecular volume of the substituents will not be sufficiently strong to bring the reacting groups close enough and consequently it is to be expected that the tendency towards ring-formation in these cases will be very small, if it exists at all. In this connection it may be mentioned that (Simonsen, *J. Chem. Soc.*, 1908, 93, 1786) observed that the keto-ester (III) on hydrolysis with hydrochloric acid gave γ-acetylbutyric acid (IV), whereas ethyl α-cyano-γ-acetyl-ββ-dimethylbutyrate (V), on similar treatment gave the dilactone (VI) as the only product (Qudrat-i-Khuda, *loc. cit.*, p. 206).



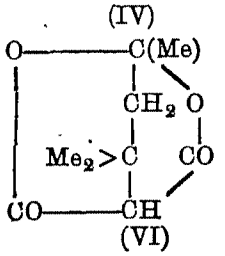
(III)



(IV)

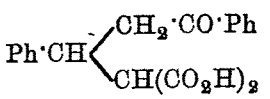


(V)

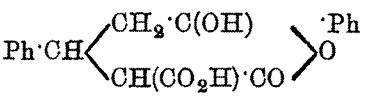


(VI)

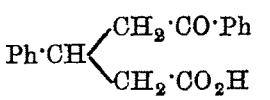
One should, therefore, expect that α-carboxy-γ-benzoyl-β-phenylbutyric acid (VII) will also exhibit properties different from those of the acids (I) in so far as the tautomeric character of the acid is concerned, and instead of the ring or the lactol form (VIII) it will exist preferably in the open-chain keto-form ; and in that case if the acid were to be heated above its melting point, unlike its isomer (I), it will yield the monobasic acid (IX) alone with the loss of carbon dioxide. And on similar considerations it may be concluded that in the keto-acid (IX) there will be very little tendency to undergo the tautomeric change to enable it to exist as the lactol (X) in the free state.



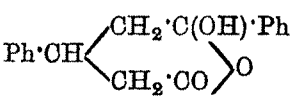
(VII)



(VIII)



(IX)

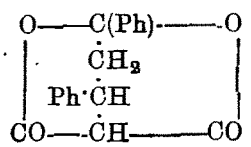


(X)

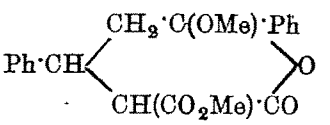
In a recent publication (Barat, *J. Indian Chem. Soc.*, 1930, 7, 321) describes the acid (VII) as the lactol acid (VIII), assigns the ring formula (X) to the keto-monobasic acid (IX) and goes on generalising the same conclusion for a series of acids of similar constitution. It appeared to the author rather peculiar that this should be the case. And hence although it formed a part of the original scheme to study the behaviour of these acids along with other monosubstituted acids of this type, it was thought desirable to examine the constitution of at least some of these acids without further delay. A study has accordingly been made into the constitution of α-carboxy-γ-benzoyl-β-phenylbutyric and α-carboxy-γ-acetyl-β-phenylbutyric acids and it is found that the observations of Barat are inaccurate and his conclusions appear to be based on an imperfect knowledge of the author's work on keto-lactol tautomerism. It may be mentioned here that this work is being continued in extension of the series of papers already published by the present author and that the former may not extend the studies of

these acids and the products of their bromination specially in these lines.

It is an obvious fact that δ-hydroxy acids undergo decomposition very readily with the formation of lactones (compare Qudrat-i-Khuda, *loc. cit.*, p. 201). Hence the acid (VII), if it were to exist as (VIII), should yield the corresponding dilactone (XI), on being heated alone, as the only product of decomposition. But the experimental observations are contrary to this expectation ; no neutral product could be isolated by the decomposition of the acid (VII), which on heating loses carbon dioxide and is completely converted into the keto-monobasic acid (IX). An attempt to convert the dibasic acid (VII) into the corresponding dilactone with dehydrating agents, such as acetyl chloride was unsuccessful, the acid after being refluxed with an excess of the reagent was recovered unchanged, thus proving that the carbonyl and the carboxyl groups in the molecule are so far apart that there is hardly any tendency here towards ring formation ; had it existed in the lactol form (VIII) it should have given a dilactone or else an acetyl derivative but the acid recovered on pouring the above reaction mixture into water, melted at the same temperature as that with which the start was made. Moreover this acid on esterification with methyl alcoholic sulphuric acid yielded the normal ester, m.p. 108°, identical with the product of condensation of dimethyl malonate and styrylphenylketone and not the methoxy ester (XII), which should result from (VIII).



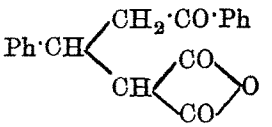
(XI)



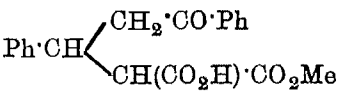
(XII)

Mannich aud Butz (*Ber.*, 1929, **62**, 456) prepared a neutral product from the dicarboxylic acid (VII) with thionyl chloride and they described it as the anhydride (XIII). This, however, might have been the dilactone (XI) but its reactions as described by them are not shared by the latter. This neutral product, for example, when boiled with absolute alcohol yields the acid ester (XIV) and with ammonia the amic acid (XV) is obtained; the dilactones so far known do not undergo such decompositions. These observations may

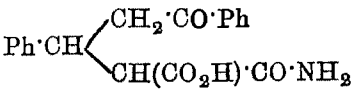
be taken as lending further support to the fact that the acid (VII) is not capable of existing in the lactol modification (VIII) at all.



(XIII)



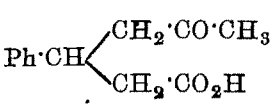
(XIV)



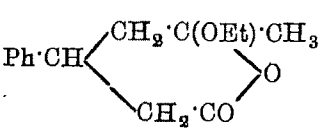
(XV)

Barat's deductions regarding the ring structure of the keto-acid (IX) appear to be based on the observation that the keto-monobasic acid (IX) did not dissolve in a solution of sodium bicarbonate but a sample of this acid prepared from the dibasic acid (VII) by decomposition is now found to dissolve completely in this solvent, only that the acid should be powdered well before being treated with the solvent. The acid obtained from the bicarbonate solution on acidification melts at the same temperature as the original acid.

A similar acid, γ-acetyl-β-phenylbutyric acid (XVI) has been described by Vorländer and Knotzsch (*Annalen*, 1897, **294**, 317) who prepared its oxime, also esterified the acid with alcoholic mineral acid and obtained the normal ester, which yielded phenyldihydroresorcinol after the necessary treatment. If the acid were to exist in the isomeric lactol form, here also, instead of the normal ester, the ethoxy ester (XVII) should have resulted on esterification, which would be incapable of giving the dihydroresorcinol derivative. The acid (XVI) has also been prepared and found to be soluble in sodium bicarbonate solution like its other homologue. It may, therefore, be concluded that the assumption of a ring structure for these and similar acids is untenable.



(XVI)



(XVII)

For the preparation of the acid (VII), the corresponding dimethyl ester was hydrolysed with 15% potassium hydroxide solution, the ester being very conveniently prepared by the method described in the experimental portion.

Experimental.

Dimethyl α-Carboxy-γ-benzoyl-β-phenylbutyrate.—Sodium (0·2 g.) was dissolved in 30 c.c. of methyl alcohol and dimethyl malonate (13 g.) was poured into this. Styrylphenylketone (20 g.) was then added to the mixture and the whole was shaken vigorously. In two to three minutes the ketone goes into solution and the mixture becomes hot ; crystals then begin to separate and the whole sets to a solid mass. It was left overnight and the solid was then filtered off, washed first with a small amount of methyl alcohol and then throughly with water. The ester crystallises well from alcohol and melts at 108° (yield 26·5 g.). The *semicarbazone* separates on heating a solution of semicarbazide acetate and the keto-ester for about three quarters of an hour on the water-bath. It crystallises from dilute alcohol or a mixture of benzene and petroleum and melts at 143°. (Found: C, 64·0; H, 5·6. $C_{21}H_{23}O_5N_3$ requires C, 63·5; H, 5·7 per cent.).

α-Carboxy-γ-benzoyl-β-phenylbutyric Acid.—The above ester (10 g.) was mixed with potassium hydroxide (6 g.) in 20 c.c. of water and 12 c.c. of alcohol. The mixture was heated under reflux for ¾—1 hour, then cooled and diluted largely with water. The smell of styrylphenylketone was perceptible at this stage and a small amount of yellow precipitate was formed, probably due to reversible decomposition in the presence of alkali. The solution was filtered off and acidified with hydrochloric acid, when the acid (VII) was precipitated out. It was filtered, washed and crystallised from aqueous alcohol, a mixture of chloroform and acetone or benzene and methyl alcohol, when it melted at 148° (decomp.) (yield 7·8 g.).

Behaviour of the Acid (VII) *on Heating.*—The acid (4·5 g.) was heated alone at 160-70° for about half an hour when the decomposition was complete. The melt was cooled and treated with a solution of sodium carbonate, in which it dissolved completely. The acid was precipitated with hydrochloric acid, filtered, washed and

dried when it weighed 8·2 g. It crystallises well from dilute acetic acid and melts at 160°. (Found: M. W. by titration, 267. Calc. M.W. 268). The *semicarbazone* separates from alcohol and melts at 220°. (Found: C, 66·8; H, 5·9. $C_{18}H_{19}O_3N_3$ requires C, 66·5; H, 5·8 per cent.). (Barat gives the melting point as 215° and no analysis ; the semicarbazone melting at this temperature appears to contain some unchanged acid along with it which is rather difficult to separate).

Dimethyl α-Carboxy-γ-acetyl-β-phenylbutyrate.—Styrylmethylketone (14 g.) was added to a mixture of dimethyl malonate (13·5 g.) and a solution of sodium (0·2 g.) in dry methyl alcohol (40 c.c.). The mixture was shaken and in a few minutes the solution became warm; this was then heated on the water-bath for an hour and a half, allowed to stand overnight and then the solvent removed by evaporation. The residue was diluted with water, the oily precipitate taken up in ether, dried and the solvent evaporated off slowly, when some solid separated in beautiful rhombic cubes. This was triturated with petroleum (b. p. 75-95°) and filtered off. The ester crystallises from a mixture of ether and petroleum and melts at 65° (yield 19·5 g.) (compare Kohler and Allen, *J. Amer. Chem. Soc.*, 1923, **45**, 1987). The *semicarbazone* crystallises from very dilute alcohol and melts at 118°. (Found: C, 57·5; H, 6·0. $C_{16}H_{21}O_5N_3$ requires C, 57·3; H, 6·2 per cent.).

α-Carboxy-γ-acetyl-β-phenylbutyric acid was prepared by hydrolysing the above ester (10 g.) with a solution of potassium hydroxide (5 g.) in 30 c.c. of water and 10 c.c. of alcohol. It was warmed to make the solution homogeneous and then left at the ordinary temperature for about 20 hours. The alkaline solution was diluted, extracted with ether, then acidified and the solution saturated with ammonium chloride when the acid was precipitated as an oil; this was taken up in ether, dried and the solvent removed. The residual oil solidified on leaving in an evacuated desiccator. It crystallises in slender silky needles from a mixture of ether and petroleum and melts at 115°. (Found: C, 62·6; H, 5·4. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6 per cent.). (compare Vorländer and Knotzsch, *loc. cit.*). The acid was recovered unchanged after being treated with acetyl chloride.

The above dibasic acid decomposes completely on being heated at 160-65° for about two hours with the elimination of carbon

dioxide only. The melt solidified on cooling and dissolved completely in a solution of sodium carbonate from which γ-acetyl-β-phenylbutyric acid was obtained on acidification. It crystallises in clusters of flattened needles from a mixture of benzene and petroleum (b. p. 75-95° and melts at 85°. (Found: M.W. by titration, 206. Calc. M.W. 206). The acid dissolves completely in a solution of sodium bicarbonate and gives a *semicarbazone* which crystallises from dilute alcohol in nodules and melts at 171·5°. (Found: C, 59·1; H, 6·3. $C_{13}H_{17}O_3N_3$ requires C, 59·3; H, 6·4 per cent.).

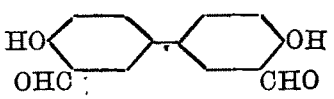
ORGANIC CHEMISTRY LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Received February 18, 1931.

4 :4′-Dihydroxydiphenyl-3 :3′-dialdehyde (*Bis*-salicylaldehyde) and its Derivatives.

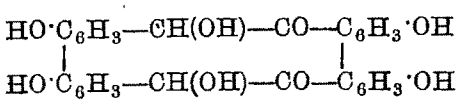
By Rajendra Nath Sen and Sorojendu Dutt.

4 :4′-Dihydroxydiphenyl-3:3′-dialdehyde (I) has now been prepared for the first time by the application of Reimer and Tiemann's reaction to *pp*′-dihydroxydiphenyl (yield 50 per cent.) using chloroform mixed with alcohol (1 :4). It is a yellow microcrystalline powder m.p. 185°, gives a dibenzoyl derivative and a diphenylhydrazone, a dioxime and a disemicarbazone. It also forms a bisulphite compound in alcoholic solution.

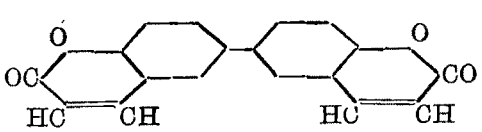


(I)

It undergoes the benzoin condensation in the usual manner producing compound (II) and also reacts with acetone in the presence of 40 per cent. sodium hydroxide solution. When heated with sodium acetate and acetic anhydride, the dialdehyde produces 6 :6′-dicoumaryl (III), identical with the compound prepared by Sen and Chakravarti from 6-iodocoumarin by heating with copper powder (*private communication*).



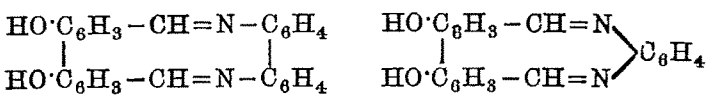
(II)



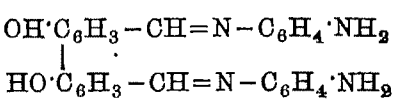
(III)

Bis-salicylaldehyde, like 6-aldehydocoumarin, aldehydophenolphthalein and aldehydofluorescein (Sen and Chakravarti, *J. Amer. Chem. Soc.*, 1928, **50**, 2428; Sen and Kar, *J. Indian Chem. Soc.*,

1929, **6**, 54; Sen and Banerjee, *ibid*, 1929, **6**, 505), gives rise to various interesting dyes with multiple chromophores by its condensation with different aromatic amino- and hydroxy-compounds. Azomethine compounds have been obtained by condensing the aldehyde with mono- and di-amines: Two molecules of a monoamine and one molecule of a diamine ordinarily react with one molecule of the aldehyde, ring compounds being obtained with benzidine (IV) and with *o*- and *p*-phenylenediamines (V). In the case of *m*-phenylenediamine, however, two molecules of the amine condense with one molecule of the aldehyde, the presence of free amino-groups in the product (VI) being proved by diazotisation.



(IV) (V)



(VI)

Pyronine dyes have been obtained by condensing a molecule of the aldehyde with four molecules of (*a*) diethyl-*m*-aminophenol, (*b*) resorcinol and (*c*) pyrogallol in the presence of sulphuric acid (*d* 1·84) in the manner described by Sen and Sinha (*J. Amer. Chem. Soc.*, 1923, **45**, 2984). The diethyl-*m*-aminophenol condensation product is soluble both in acids and alkalis and dyes wool and silk a violet shade; the pyrogallol compound gives an octapotassium salt and is polygenetic (brownish-black with iron mordant and olive-green with chromium mordant), while the resorcinol compound gives a tetrapotassium salt dyeing an orange shade, and an octabromo-derivative, which dyes wool and silk a beautiful red shade.

Triphenylmethane dyes have been obtained by condensing the aldehyde with (*a*) dimethylaniline and (*b*) *o*-cresotinic acid; the leuco-bases, on oxidation, give a fine bluish dye in the first case and a mordant dye (yellowish-red with aluminium mordant) in the second case.

Incidentally it may also be mentioned that by the application of Reimer and Tiemann's reaction with carbon tetrachloride on an alkaline solution of *pp'*-dihydroxydiphenyl, a dicarboxylic acid, indentical with the acid prepared from *bis*-anthranilic acid (Bülow and Reden, *Ber.*, 1898, **31**, 2577), has been obtained.

EXPERIMENTAL.

Bis-*salicylaldehyde* (*4 :4′-Dihydroxydiphenyl-3 :3′-dialdehyde*).—To a solution of *pp′*-dihydroxydiphenyl (15 g.) in caustic soda solution (30 g. in 70 c.c. water) heated on a water-bath at 40-50°, and stirred with a mechanical stirrer a mixture of alcohol and chloroform (4 :1; 25 c.c. chloroform in all) is added drop by drop and the solution kept at this temperature with continuous stirring for twelve hours. The excess of chloroform being distilled off, the solution is cooled, diluted with water and acidified with acetic acid. The precipitate is filtered off, washed with water and dried. It is extracted repeatedly with ether, in which the parent phenol is readily soluble while the aldehyde is quite insoluble. It is finally crystallised from a mixture of acetone and alcohol (6 :1), in yellow microcrystalline powder melting at 185° (yield, 8 g.). It is readily soluble in acetone and pyridine, less so in alcohol and glacial acetic acid, insoluble in ether, chloroform, benzene, carbon disulphide and carbon tetrachloride. It dissolves in aqueous caustic alkalis and alkaline carbonates (red solution). (Found: C, 68·95, 69·24; H, 4·8, 4·18. $C_{14}H_{10}O_4$ requires C, 69·42; H, 4·10 per cent.).

The *diphenylhydrazone*, prepared in the usual manner, crystallises from dilute pyridine in yellow microcrystalline powder melting at 215°. It dissolves in caustic alkalis and sparingly in alkaline carbonates (yellowish-brown solution). (Found: N, 13·42; 13·5. $C_{26}H_{22}O_2N_4$ requires N, 13·27 per cent.).

The *disemicarbazone*, prepared as usual, is obtained from pyridine in the form of yellow powder; it does not melt up to 300°. (Found: N, 23·4, 23·7. $C_{16}H_{16}O_4N_6$ requires N, 23·6 per cent.).

The *dioxime*, prepared as usual, is obtained from absolute alcohol in the form of dark yellow powder which does not melt up to 300°. (Found: N, 10·47. $C_{14}H_{12}O_4N_2$ requires N, 10·3 per cent.).

The *dibenzoyl* derivative, prepared by Schotten-Bauman's method, crystallises from ethyl acetate as large feathery crystals melting at 100°. (Found: C, 74·4. H, 4·02. $C_{28}H_{18}O_6$ requires C, 74·6; H, 4·00 per cent.).

Benzoin Condensation.—A solution of the aldehyde (3 g.) in alcohol (20 c.c.) with 1 per cent. aqueous alcoholic solution of potassium cyanide (10 c.c.) is heated on the water-bath (6 hours). The solution on acidification with hydrochloric acid, gives a yellow precipitate which is filtered off and washed with water. It is finally crystallised from alcohol in the form of reddish-brown microcrystal-

line powder, which does not melt up to 303°. It readily reduces Fehling's solution and dissolves in dilute caustic alkalis and alkaline carbonates. (Found: C, 69·49; H, 4·13. $C_{28}H_{20}O_8$ requires C, 69·42; H, 4·13 per cent.).

Condensation with Acetone.—To a solution of the aldehyde (2 g.), acetone (10 c.c.) and caustic soda solution (40 per cent., 10 c.c.) are added and the solution left overnight; the solid, that separates, is filtered off and is obtained in the form of a deep red powder from glacial acetic acid, not melting up to 300°. (Found: C, 74·42, 74·23; H, 5·59, 5·58. $C_{20}H_{18}O_4$ requires C, 74·53; H, 5·59 per cent.).

6:6′-*Dicoumaryl.*—The aldehyde (4 g.) is moistened with acetic anhydride (10 c.c.) in a dry conical flask and fused sodium acetate (3 g.) is added and the mass is stirred with a glass rod with a few crystals of iodine. 1 C.c. of pyridine is added and the flask is then heated with an air condenser in an oil-bath at 120-30° for 2 hours. The temperature is then raised to 190-200° and maintained there for 8 hours. The mass is then cooled, washed with water and is extracted repeatedly with sodium carbonate solution which dissolved the unchanged aldehyde. It is then dissolved in caustic soda solution and carbon dioxide is passed through it which further precipitates the remaining quantity of the aldehyde. The process is repeated until no more precipitation takes place with carbon dioxide. The filtrate is then boild to expel carbon dioxide and is acidified with dilute hydrochloric acid, when the coumarin compound is precipitated. It is dissolved in pyridine and is precipitated by pouring the solution into a large volume of water and is finally crystallised from dilute pyridine in the form of yellowish-brown powder which decomposes above 200° (yield 40 per cent.). The product is soluble in pyridine, less so in chloroform, acetone, methyl and ethyl alcohols. It is insoluble in carbon bisulphide, ether, benzene, carbon tetrachloride, petroleum, ether and water. (Found: C, 74·5, 74·3; H, 3·5, 3·4. $C_{18}H_{10}O_4$ requires C, 74·4; H, 3·4 per cent.).

Azomethine Derivatives.

The general method of preparation of these compounds is to add an alcoholic solution of an amine to an alcoholic solution of the aldehyde; crystals often separate on mixing the hot solutions. The reaction is finished by heating the solution on the water-bath sometimes with the addition of a little fused sodium acetate. The

product is washed with dilute acids and crystallised. The yield is generaly theoretical. The azomethine compounds are described in Table A.

Pyronine and Triphenylmethane Dyes.

The general method of preparation of these dyes is to treat the mixture of the aldehyde (1 mol.) and the hydroxy-compound (4 mols.) with concentrated sulphuric acid (*d* 1·84) sufficient to make the mixture a paste. The mixture is then heated at about 120-30° for sometime, when sulphur dioxide escapes. The product is then isolated by pouring into water and purified by acid and alkali treatment. It is finally crystallised from a suitable solvent. The condensation with dimethylaniline is effected in the presence of hydrochloric acid. Compounds of these series are listed in Table B.

4 : 4′-*Dihydroxydiphenyl*-3 : 3′-*dicarboxylic Acid.*—The preparation of this compound is the same as that of the dialdehyde but instead of chloroform carbon tetrachloride has been used. The crude product is purified by treatment with acetic acid in the cold in which the acid is readily soluble whilst the diphenol is very sparingly soluble. The solution is then poured into water, the precipitate is allowed to settle and filtered. It is finally crystallised from acetic acid in the form of yellow powder which melts slightly above 300° The yield is 40 per cent.

TABLE A.

Azomethine Compounds.

Formulae.	Method of preparation (A = The aldehyde).	P.c. of N. Calc.	P.c. of N. Found.	Appearance and melting point.	Remarks.
$C_{16}H_{10}O_2N_2$	A + aniline + sodium acetate.	7·1	7·8 6·96	Reddish-brown powder, not melting up to 300°.	Crystallises from amyl alcohol. Soluble in alcohol, acetone, ethyl acetate and acetic acid.
$C_{28}H_{24}O_2N_2$	A + *p*-toluidine + sodium acetate.	6·6	6·3 6·9	Small red needles softening at 175°.	Crystallises from pyridine. Sparingly soluble in alcohol and acetone.
$C_{36}H_{28}O_2N_6$	A + aminoazobenzene.	14	14·3 13·9	Red microcrystalline powder, m.p. 260°.	Crystallises from pyridine; Sparingly soluble in acetic acid, alcohol and acetone.
$C_{26}H_{18}O_2N_2$	A (1 mol.) + benzidine (1 mol.).	7·2	6·95 6·89	Reddish-brown powder not melting up to 300°.	Crystallises from aniline; soluble in pyridine and insoluble in alcohol and acetone.
$C_{20}H_{14}O_2N_2$	A (1 mol.) + *p*-phenylenediamine (1 mol.).	8·9	8·5 8·7	,,	Crystallises from aniline, soluble in pyridine and insoluble in benzene, nitrobenzene, alcohol and acetone.
$C_{20}H_{14}O_2N_2$	A (1 mol.) + *o*-phenylenediamine (1 mol.).	8·9	8·63	Dark red powder, not melting up to 300°.	Crystallises from aniline, soluble in pyridine and aniline.
$C_{26}H_{22}O_2N_4$	A (1 mol.) + *m*-phenylenediamine (2 mols.).	13·3	13·4	Does not melt up to 300°.	Soluble in aniline and pyridine; insoluble in nitrobenzene, alcohol and acetone. The presence of the free amino-groups is proved by diazotisation.

TABLE B.

Pyronine Dyes.

Formula.	Method of preparation (A = The aldehyde).	M. p.	Shade on wool and silk.	Analysis : Calc.	Found.	Remarks.
$C_{54}H_{62}O_6N_4$	A(1 mol.) + diethyl-*m*-aminophenol (4 mol.) + H_2SO_4 (*d* 1·84) at 120°-130°.	Does not melt up to 300°.	Violet	N,6·5	N, 6·7 6·8	Violet powder from dilute alcohol, soluble in acids and in alkalis.
$C_{36}H_{24}O_6$	A(1 mol.) + resorcinol (4 mol.) + H_2SO_4 on the water-bath for 6 hrs.	,,	Orange	C,75·2 H,3·63	C,75·09 H,3·66	Red microcrystalline powder from dilute alcohol, alkaline solution exhibiting a green fluorescence.
$C_{38}H_{18}O_4K_4$	Prepared in the usual manner.	—	—	K,20·6	K,20·2	Long red needles from water.
$C_{36}H_{14}O_6Br_6$	By adding bromine to a solution of the substance.	,,	Brilliant red	Br, 51·6	Br, 51·2	Deep red microcrystalline powder.
$C_{36}H_{22}O_{12}$	A(1 mol.) + pyrogallol (4 mol.) + H_2SO_4 on the water-bath for 6 hrs.	,,	Black (iron mordant), green (chromium mordant).	C,68·06 H,3·3	C,68·2 H,3·3	Greyish-black powder from alcohol.
$C_{36}H_{14}O_{12}K_8$	...	—	—	K,32·08	K,32·2	—

Triphenylmethane Dyes.

$C_{46}H_{50}O_2N_4$	A(1 mol.) + dimethylaniline (4 mol.) + HCl on the water-bath for 30 hrs.	Does not melt up to 300°.	Bluish-green by the oxidised base.	N,8·11	N,8·8, 8·2	Star-shaped crystals from alcohol, oxidised with PbO_2 in the usual manner.
$C_{46}H_{38}O_{14}$	A(1 mol.) + o-cresotinic acid (4 mol.) + H_2SO_4 in the cold for 24 hrs.	Decomposed at 225°.	Yellowish-red (iron, aluminium and chromium mordant) by the oxidised base.	C,67·8 H,4·7	C,67·61 H,4·7	Brown powder by precipitation from the ethereal solution by benzene. Oxidised with nitrosyl sulphate.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Received January 19, 1931.

Constitution of the Active Principle of *Embelia Ribes*. Part II.

By Ramjee Kaul, Amaresh Chandra Ray and Sikhibhushan Dutt.

In Part I of this series (*J. Indian Chem. Soc.*, 1926, **6**, 577), embelin, the active principle of *Embelia ribes*, was isolated in a perfectly pure and crystalline form and a number of its important derivatives prepared and analysed. The results proved beyond doubt that embelin, which has the formula $C_{18}H_{28}O_4$, contains two highly reactive hydroxy groups giving most of the reactions of a phenolic nature and two ketonic groups. The hydroxy groups were also shown to undergo interesting keto-enol tautomerism, so that, under suitable conditions, embelin behaved as if it had four ketonic groups.

In the present investigation, embelin has been shown to contain two reactive methylene groups since it condenses with two molecules of aldehydes and two molecules of nitroso-compounds in presence of concentrated sulphuric acid, alcoholic sulphuric acid or hydrogen chloride and glacial acetic acid, yielding crystalline products. The condensation products with aldehydes which are generally orange or yellow in colour crystallise with a molecule of water of crystallisation which is lost on continued heating at 120° with partial decomposition of the molecule and also at 70° in vacuum without decomposition. These compounds which are somewhat analogous to stilbene derivatives, yield dibromides with bromine in chloroform or carbon tetrachloride and regenerate the aldehyde by the action of dilute potassium permanganate. But in the latter case the embelin molecule is destroyed by oxidation. The condensation products with nitroso-compounds which are generally dark in colour, are rather easily attacked by even weak reducing agents, regenerating embelin, together with the formation of an aromatic amine corresponding to the original nitroso-derivative. Thus the condensation product of embelin with *p*-nitrosophenol on reduction by zinc dust and caustic soda yields embelin and *p*-aminophenol. Stronger reducing agents yield dihydroembelin together with an aromatic amine. In both these types of condensations, it has been possible to isolate a few mono derivatives

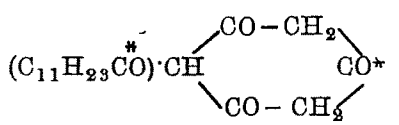
in which embelin has condensed with only one molecule of aldehyde or nitroso-compound. The following aldehydes and nitroso-compounds have been condensed with embelin: benzaldehyde, salicylaldehyde, anisaldehyde, *p*-toluic aldehyde, vanillin, paraldehyde and butyric aldehyde; nitrosobenzene, *p*-nitrosophenol, nitrosoresorcinol, nitrosodimethylaniline and nitroso-β-naphthol.

Embelin was also found to react with ethyl formate and nitrous acid but the condensation product could not be isolated in pure form.

In this connection it was found that embelin undergoes oxidation by nitric acid with formation of *n*-lauric acid together with smaller quantities of oxalic and malonic acids. The formation of *n*-lauric acid somewhat contradicts the results previously obtained by the present authors (Part I, *loc. cit.*), where *iso*lauric acid was isolated. This led the authors to reinvestigate the action of potassium permanganate with a large quantity (50 g.) of the material. A white crystalline substance was obtained (12 g.) which on repeated recrystallisation from methyl alcohol finally melted at 43°, and was found to be identical with *n*-lauric acid (mixed m.p.). From the alcoholic mother-liquors, smaller quantities (4·3 g.) of another acid were isolated, melting at 34-35°, and which apparently seemed to have properties somewhat different from those of *n*-lauric acid. It is just possible that it might be identical with the little known *iso*lauric acid or it may be a slightly impure specimen of *n*-lauric acid. On account of the impossibility of securing a genuine specimen of *iso*-lauric acid, its identity could not be definitely established.

From the foregoing results it is quite evident that embelin contains two reactive methylene groups, which fact also accounts for the interesting keto-enol tautomerism which embelin undergoes.

This together with the interesting fact that embelin is very easily attacked by oxidising agents with formation of mainly *n*-lauric acid together with smaller quantities of oxalic and malonic acids, lead us to assign the following provisional formula to embelin



in which the portion within brackets indicates the lauric acid residue, the CO-groups marked by asterisks are true ketonic groups, and the

remaining CO-groups are those which undergo keto-enol tautomerism. Such a formula clearly explains all the observed properties of embelin. Attempts are being made to corroborate such a formula by synthesis.

EXPERIMENTAL.

Condensation of embelin with aldehydes were carried out either by alcoholic sulphuric acid (method I) or by alcoholic hydrogen chloride (method II). Condensations with nitroso-compounds were done by a mixture of absolute alcohol and glacial acetic acid (1:1 by vol., method III). For the sake of abbreviation an example of each of these methods is given, after which the rest of the results is summarised in tabular forms.

Method I. *Benzylidene-embelin*, $C_{18}H_{26}O_4:CHC_6H_5$, H_2O.—A mixture of embelin (3 g.) and freshly distilled benzaldehyde (2 g) was heated under reflux for three hours on the water-bath with 50 c.c. of absolute alcohol and 5 c.c. of concentrated sulphuric acid. The reaction mixture was poured into water and boiled for some time in an open dish in order to drive off the excess of benzaldehyde. It was then filtered and the residue crystallised from dilute alcohol in pale yellow needles melting at 112°.

The substance is fairly soluble in most of the organic solvents and also in strong caustic alkalis. Treated with concentrated sulphuric acid it partly dissolves with a reddish colour and partly charrs forming a black carbonacious mass. On treatment with dilute potassium permanganate acidified with dilute sulphuric acid, the odour of benzaldehyde is at once perceptible. By the action of alkaline permanganate, it is completely broken down into benzoic, oxalic, malonic and lauric acids. (Found: C, 71·83; H, 8·2; loss on heating at 70°/40 mm. for six hours, 4·6. $C_{25}H_{32}O_4,H_2O$ requires C,72·2; H, 8·2; H_2O, 4·3 per cent.).

Method II. *Dibenzylidene-embelin*, $C_{18}H_{24}O_4:(CHC_6H_5)_2$.—A mixture of benzaldehyde (10 g.) and embelin (3 g.) dissolved in 100 c.c. absolute alcohol was saturated with dry hydrogen chloride at the ordinary temperature. On allowing the mixture to stand for 24 hours, the colour of the solution became dark red and a little dibenzylidene-embelin crystallised out. The alcohol was then evaporated and the excess of benzaldehyde removed in steam. The dark brown crystalline product thus obtained was digested with 40% sodium hydroxide in order to free it from the traces of mono-benzylidene

derivative, and the residue crystallised from 70% acetic acid in brownish-yellow needles, m.p. 142°.

The substance is much less soluble in the ordinary organic solvents than the foregoing mono-derivative, and unlike the latter substance it is insoluble in caustic alkalis. It dissolves in concentrated sulphuric acid with a reddish-violet colour. (Found: C,78·95; H, 7·4. $C_{32}H_{36}O_4$ requires C,79·3; H,7·4 per cent.).

Method III. *Bis-phenyliminoembelin*, $C_{18}H_{24}O_4$: $(N{\cdot}C_6H_5)_2$.—A mixture of embelin (3 g.) and nitrosobenzene (2 g.), dissolved in a mixture of alcohol and acetic acid (1:1, 100 c.c.), was heated on the water-bath for one hour. On pouring into water a dark brown mass separated which was filtered off and crystallised from dilute alcohol (animal charcoal) in buff coloured needles, m.p. 195° (decomp.). It is fairly soluble in alcohol and acetic acid, and insoluble in chloroform, benzene, water and caustic alkalis. It does not give any colour reaction with concentrated sulphuric acid. (Found: N,6·05. $C_{30}H_{34}O_4N_2$ requires N, 5·7 per cent.).

Action of Ethyl Formate on Embelin.—Embelin (5 g.) dissolved in dry toluene (250 c.c.) was treated with ethyl formate (3 g.) and finely divided sodium (0·75 g.). The mixture was kept in a refrigerator for 12 hours and then warmed on the water-bath for 2 hours. The solution gradually assumed a blood-red colour and finally set to a crimson-coloured jelly on cooling. The mixture was then acidified with dilute acetic acid and the toluene distilled off in steam. The viscous residue which on cooling became a soft, dark brown, sticky and exceedingly tenacious mass, could not be crystallised or purified for analysis. It dissolves in caustic alkalis with a blood-red colour and is much more soluble than embelin in the ordinary organic solvents. The general properties are also quite different.

Action of Nitrous Acid on Embelin.—Embelin (3 g.) dissolved in 30 c.c. concentrated sulphuric acid was treated with finely divided sodium nitrite (1 g.). The mixture was cooled in ice while being vigorously stirred, and pieces of ice were gradually added until the precipitation of the *iso*nitroso-compound was complete. The substance, which is a bright yellow crystalline compound dissolving in dilute sodium hydroxide with an orange colour, is only stable at the temperature of ice, since on allowing it to attain ordinary temperature, it spontaneously splits off nitrous acid with regeneration of embelin attended with partial oxidation of the latter. The same thing happens if any attempt is made to crystallise it from organic

solvents. On being rapidly heated it burns with emission of sparks. By warming the substance with alcohol, the odour of acetaldehyde becomes at once perceptible.

Action of dilute Nitric Acid on Embelin.—Embelin (20 g.) was heated with dilute nitric acid (250 c.c., *d* 1·15) on the water-bath for 20 hours. The embelin gradually disappeared and a pale yellow oil was formed, which on cooling solidified to a colourless waxy solid. This was filtered off, washed with water and distilled in steam to free it from traces of volatile fatty acids. It was then repeatedly crystallised from methyl alcohol and finally obtained in the form of lustrous plates melting at 43°, and was found to be identical with *n*-lauric acid (mixed m.p.) (yield, 1·9 g.). The alcoholic mother-liquors on collection, evaporation to a small volume and precipitation by water yielded 1·1 g. of another acid melting at 34-35°, whose identity could not be definitely established. It was practically the same compound as that obtained by the action of potassium permanganate on embelin, and described in a previous communication (*J. Indian Chem. Soc.*, 1929 **6**, 586) as *iso*lauric acid. It may also be a slightly impure specimen of *n*-lauric acid from which the impurity could not be eliminated by repeated crystallisations.

The nitric acid mother-liquors on neutralisation by sodium carbonate, evaporation to a small volume and treatment with calcium chloride yielded a heavy white precipitate which was found to be mainly calcium oxalate mixed with a little calcium malonate. No other acid could be detected.

Condensation Products of Embelin with Aldehydes and Nitroso-Compounds.

Name. (E = embelin).	Formula.	Method of preparation.	Constituents (E = embelin).	Appearance and m.p.	Crystallised from.	Analysis. (theoretical values in brackets).
Disalicylidene – E	$C_{32}H_{36}O_6$, H_2O	I	Salicylaldehyde (2 mols.) + E	Orange-yellow needles, m.p. 152°	Dil. alcohol	C, 71·4(71·9); H, 6·9(7·1).
Dianisylidene – E	$C_{34}H_{40}O_6$, H_2O	I	Anisaldehyde (2 mols.) + E	Orage-needles, m.p. 167°	,, ,,	C, 72·3(72·5); H, 7·5(7·4),
Divanillidene – E	$C_{34}H_{40}O_8$, H_2O	I	Vanillin (2 mols.) + E	Orange-red needles, m.p. 230°	70% acetic acid	C, 67·6(67·9); H, 7·8(7·8).
Di-*p*-methylbenzylidene – E	$C_{34}H_{40}O_4$, H_2O	II	*p*-Toluic aldehyde (2 mols.) + E	Orangeneedles, m p. 244°	Dil. alcohol	C, 76·7(76·9); H, 7·8(7·9)
Diacetylidene – E	$C_{28}H_{32}O_4$, H_2O	II	Paraldehyde (1 mol.) + E	Yellow needles, m.p. 123°	Dil. acetone	C, 69·3(69·3); H, 8·5(8·5)
Dibutylidene – E	$C_{36}H_{40}O_4$, H_2O	II	Butyric aldehyde (2 mols.) + E	Brown-yellow needles, m.y. 120°	Dil. alcohol	C, 70·8(71·18); H, 9·7(9·8).
Bis-*p*-hydroxyphenylimino – E	$C_{30}H_{34}O_6N_2$	III	*p*-Nitrosophenol (2 mols.) + E	Brown needles, m.p. 207°	Acetic acid	N, 5·2(5·4)
Bis-*p*-dimethylaminophenyl-imino – E	$C_{34}H_{44}O_4N_4$	III	*p*-Nitrosodimethyl-aniline (2 mols.) + E	Dark brown leaflets, m.p. above 290°	Alcohol	N, 9·6(9·9)
p-Dimethylaminophenyl-imino – E	$C_{26}H_{36}O_4N_2$	II	*p*-Nitrosodimethyl-aniline (2 mols.) + E	Brown crystalline powder, m p. above 290°	Dil. alcohol	N, 6·3(6·1)
Bis-2 :4-dihydroxyphenyl-imino – E	$C_{30}H_{34}O_8N_2$	III	Mononitroso- resorcinol (2 mols.) + E	Brown powder, m.p. 230°	...	N, 5·1(5 08)
Bis-2-hydroxynaphthyl-imino – E	$C_{38}H_{38}O_6N_2$	III	Nitroso-β-naphthol (2 mols.) + E	Brown powder, m.p. above 290°	...	N, 4·09(4·5)

CHEMICAL LABORATORY, ALLAHABAD UNIVERSITY.

Received December 30, 1930.

Constitution of Embelin.

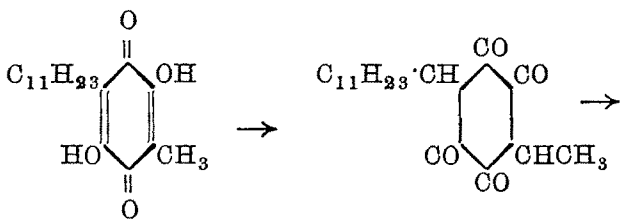
By Krishna Shrinivas Nargund and Balvant Wasudev Bhide.

Heffter and Feuerstein (*Arch. Pharm.*, 1900, **238**, 15) showed that embelin contained a side-chain, very probably $C_{11}H_{23}$ as they were able to isolate *n*-lauric acid by oxidation. They prepared a dibenzoyl derivative and showed that embelin condenses with primary amines in the same way as benzoquinone. Moreover on reduction it gives a colourless dihydroembelin which quickly oxidises in air to embelin thus showing a behaviour akin to quinone. These facts led them to assign the constitutional formula (I) to embelin. One of us (K.S.N.) and Kanga (*Proc. Indian Science Congress*, 1929, 145) proved the presence of two keto-groups in the molecule, while Kaul, Ray and Dutt (*J. Indian Chem. Soc.*, 1929, **6**, 577) observed that it behaved as if it had four keto-groups under certain conditions.

Kaul Ray and Dutt (*loc. cit.*), by oxidising embelin with fuming nitric acid, obtained *iso*lauric acid which on further oxidation gave *iso*caproic acid. Heffter and Feuerstein (*loc. cit.*) isolated *n*-lauric acid by oxidising embelin with alkaline potassium permanganate. Oxidation of embelin, either by alkaline potassium permanganate or by potassium permanganate in acetone solution, yielded the same products as obtained by Heffter and Feuerstein. Indeed, the crude acid obtained by oxidation, does melt at 35-37° as stated by Dutt and his colleagues but after a couple of crystallisations the melting point rises to 43·5° and is not diminished by the admixture of *n*-lauric acid, obtained from Kahlbaum. The oxidation of embelin under different conditions by dilute nitric acid has been very thoroughly studied by Limaye (*Proc. Indian Science Congress, Nagpur*, 1931). In addition to *n*-lauric acid he isolated *n*-lauronitrile but not *iso*-lauric acid.

A clue to the solution of this problem was afforded by the work of Fichter (*Annalen*, 1908, **361**, 363) who prepared a number of *p*-dioxyquinones and studied their hydrolysis in detail; under the conditions of experiments described by him he obtained disubstituted succinic acids. As there is a great resemblance between Fichter's

compounds and embelin we decided to study its hydrolysis. Embelin on hydrolysis by dilute sodium hydroxide gave α-ketomyristic acid, $C_{14}H_{26}O_3$, m.p. 63·8° (oxime, m.p. 95°; semicarbazone, decom. above 170°). Its constitution was proved by its oxidation to tridecoic acid, m.p. 43° (zinc salt, m.p. 128°). The melting point was considerably lowered by mixing it with *n*-lauric acid. (Mrs.) Robinson describes tridecoic acid as melting at 43°, and the zinc salt at 128° (*J. Chem. Soc.*, 1924, 125, 226). The mechanism of the formation of α-ketomyristic acid from embelin may be represented as follows:



(I)

$C_{11}H_{23}\cdot CH_2\cdot CO\cdot CO_2H$ + $CH_3CH_2\cdot CO\cdot CO_2H$

(II) (III)

Attempts were made to isolate α-ketobutyric acid (III) from the mother-liquor after separating the α-ketomyristic acid. In all cases a gum was obtained which could not be induced to crystallise from the usual solvents. We were also unable to isolate any crystalline compound after esterifying the gum.

The synthesis of embelin either from *p*-dihydroxychlorotoluquinone and undecyl chloride or from α-ketomyristic ester and α-ketobutyric ester is being attempted.

Experimental.

Embelin, m.p. 143°, used in this work was prepared by extracting the dry berries with ether followed by washing with petrol; one crystallisation from alcohol gave the pure product.

Oxidation of Embelin in Acetone Solution.—Embelin (5 g.) was dissolved in acetone (50 c.c.) and potassium permanganate (4 g.) added with stirring and cooling. The product was then diluted with water (50 c.c.) and a rapid stream of sulphur dioxide was passed

into it. The oil which separated out was removed by means of ether. After the removal of ether, a solid melting at 35-37° was obtained. It was further crystallised from alcohol when it melted at 43·5° and was identical with *n*-lauric acid obtained from Kahlbaum. Oxidation of embelin by alkaline permanganate also gave the same product. The acid was also converted into lauramide, m.p. 98°.

Hydrolysis of Embelin and Isolation of α-Ketomyristic Acid.—Embelin (5 g.) was heated with aqueous potassium hydroxide (200 c.c. of 5 per cent.) on the water-bath for four hours. The original violet colour changed to brown. On cooling, sodium ketomyristate separated out which was filtered and washed with water. It can be crystallised from hot water as a fine micro-crystalline powder and is insoluble in cold water. (Found: Na, 9·1. $C_{14}H_{25}O_3Na$ requires Na, 8·99 per cent.). Fichter recommends boiling till the solution becomes colourless. In one of our experiments even though the boiling was continued for 96 hours the product did not become colourless and the separation of α-ketomyristic acid became difficult. The sodium salt was decomposed with dilute hydrochloric acid and α-ketomyristic acid thus liberated was crystallised from light petrol as small plates, m.p. 63·8°. The acid retains the solvent somewhat tenaciously and it is necessary to keep it in vacuum over paraffin for several hours to remove the last traces of the solvent. (Found: C, 69·3; H, 10·8; equivalent, 241. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·74 per cent.; equivalent, 242).

Semicarbazone of α-Ketomyristic Acid.—The keto-acid (1·2 g.) was dissolved in alcohol and treated with semicarbazide hydrochloride (0·6 g.) and excess of sodium acetate. The mixture was warmed and then left for 24 hours. On diluting and acidifying, the semicarbazone separated as a flocculent precipitate. It is crystallised from dilute alcohol and decomposes above 170°. (Found: C, 60·08; H, 9·78; N, 13·8. $C_{15}H_{29}O_3N_3$ requires C, 60·2; H, 9·7; N, 14·0 per cent.).

Oxime of α-Ketomyristic Acid.—The keto-acid (1·2 g.) was treated in alcoholic solution with hydroxylamine hydrochloride (0·5 g.) and an excess of sodium acetate. After 24 hours the mixture was diluted with water and acidified. An oil (0·9 g.) separated which soon solidified. It crystallises from dilute alcohol in rosettes, m.p. 94-95°. (Found: N, 5·6. $C_{14}H_{27}O_3N$ requires N, 5·45 per cent.).

Oxidation of Ketomyristic Acid by Nitric Acid.—The acid (1·2 g.) was boiled with 35 c.c. of nitric acid (1:4) for 18 hours. Then 5 c.c. of fuming nitric acid were added and heating was continued for a further period of 5 hours. On cooling tridecoic acid (0·8 g.) solidified. On crystallising twice from dilute alcohol it melted at 43°. The zinc salt prepared by treating the ammonium salt with excess of zinc chloride, when crystallised twice from amyl alcohol, melted at 128°.

Oxidation of the Keto-acid by Alkaline Potassium Permanganate.—The keto-acid (1 g.) was dissolved in sodium carbonate solution (50 c.c. of 5 per cent.) and then treated with potassium permanganate (20 c.c. of 10 per cent.). It was heated on the water-bath for an hour. On filtering and acidifying an oil separated which quickly solidified. After crystallisation from alcohol it melted at 43°. The zinc salt had m.p. 128°.

In conclusion we have great pleasure in expressing our heartfelt thanks to Prof. Kanga and Mr. Limaye for their kind interest and advice during the progress of the work.

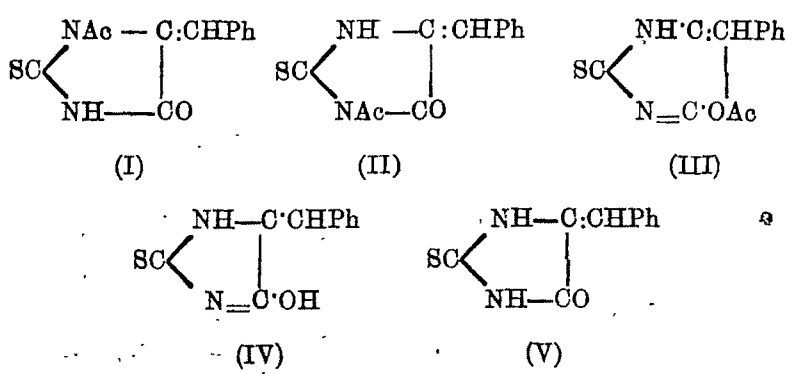
M. R. Science Institute, Ahmedabad
AND
Sir Parashurambhau College, Poona.

Received January 19, 1931.

Dyes derived from Thiohydantoin. Part II.

By Vishnu Ganesh Namjoshi and Sikhibhushan Dutt.

In Part I of this series (Pendse and Dutt, *J. Indian Chem. Soc.*, 1930, 7, 963) thiohydantoin was condensed with a number of nitroso- and *iso*nitroso-compounds resulting in products possessing interesting dyeing properties. It has now been condensed with a series of aromatic aldehydes. Condensations of thiohydantoin with benzaldehyde, anisaldehyde vanillin and piperonal seem to have been carried out (*cf.* Johnson, Wheeler and Nicolet, *J. Amer. Chem. Soc.*, 1911, **33**, 1973; Johnson and Bengis, *ibid*, 1913, **35**, 1609; Ruhemann and Stapleton, *J. Chem. Soc.*, 1900, **77**, 246). But whereas, the previous authors used glacial acetic acid and fused sodium acetate as the condensing agent, we used acetic anhydride, which brought about the condensations much more easily, but the products obtained were found to be acetyl derivatives of the condensation products, which can have three alternative constitutions. For example, the condensation product of benzaldehyde and thiohydantoin can have one of the first three alternative structures given below:—



(I) (II) (III)

(IV) (V)

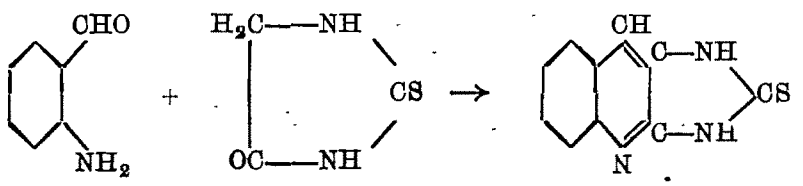
Stucture (I) is very unlikely, because in this form the acetyl group would be very unstable, since it has been found that 3-acetylthiohydantoin and 3-benzoylthiohydantoin on condensation with benzaldehyde in presence of glacial acetic acid and fused sodium

acetate, very readily suffers spliting off of the acidyl groups with formation of benzylidenethiohydantoin. Hence position 3 from which an acid group is so easily split off is very unlikely to be the place in which an acidyl group can be subsequently introduced. Then only remains structures (II) and (III) between which the latter seems to be the most likely, because from the point of view of a theory of colour advanced by one of us (Dutt, *J. Chem. Soc.*, 1926, 129, 1171; *J. Indian Chem. Soc.*, 1927, 3, 99) this structure which contains a carbon-nitrogen double bond, would be more coloured than benzylidenethiohydantoin (V) which contains a carbon-oxygen double bond whereas structure (II) would have practically the same colour as benzylidenethiohydantoin, since it contains the same type of linkage. During the course of these investigations it was found that the acetyl derivatives of the condensation products are always more coloured than the deacetylated compounds which are readily obtained by hydrolysis of the former with alkali. Hence structure (III) is the most probable configuration for the condensation products.

It was also observed that the condensation products are very easily hydrolysed by alkali and thereby revert from the acetylated enolic (III) to the free keto-type (V) *via* the intermediate unstable free enolic form (IV). However, in some instances the complete reversion took some time, whereas in some cases a fair amount of heat had to be applied during the process of crystallisation or the subsequent drying. Thus acetylbenzylidenethiohydantoin on dissolving in 20% sodium hydroxide solution rapidly undergoes hydrolysis, and the clear solution on the addition of dilute acids throws down a bright yellow precipitate, which on crystallisation from alcohol and subsequent drying in vacuum, melts at 220° on the second day, at 232-34° on the 6th day, at 242-45° on the 12th day, at 255-58° on the 18th day, 259° on the 24th day, after which the melting point remains constant. However the yellow precipitate on crystallisation from glacial acetic acid or amyl alcohol and subsequent drying in the air oven at 120°, gives a product melting at 259° in one day. In order to remove any doubt that the lower melting products might not be impure specimens of the higher melting product, all the different samples were analysed and the analytical results were found to be practically identical. From these it was concluded that the lowest melting point was that of the pure enolic compound, the intermediate values

were those of various mixtures of enol and keto types and the highest melting point was that of pure keto compound. In order to avoid a complexity of melting points, all the compounds described in this paper were prepared for a second time, twice recrystallised from glacial acetic acid and dried at 120° before the melting points were determined and recorded.

The following aromatic aldehydes have been condensed with thiohydantoin in presence of acetic anhydride and the condensation products isolated both in the acetylated enolic and free keto-forms:— benzaldehyde, *o*-, *m*-, and *p*-nitrobenzaldehyde, *o*-, *m*-, and *p*-hydroxybenzaldehyde, *m*-and *p*-amino-benzaldehyde, anisaldehyde, *β*-resorcylaldehyde, vanillin, piperonal, cinnamaldehyde and *p*-dimethylaminobenzaldehyde. The condensation product of *o*-aminobenzaldehyde has been obtained in the form of a quinoline derivative (VI).



(VI)

The same product is obtained when *o*-nitrobenzylidenethiohydantoin is reduced with tin and hydrochloric acid.

Most of the compounds described in this paper are highly coloured substances which dye wool and silk in fine shades of yellow and orange from an acid bath. They also dye cotton direct from alkaline bath containing sodium carbonate to shades which are only slightly weaker than those on wool and silk. Solutions of these substances in alkali on standing are apt to decompose due to oxidation and hydrolysis, and in strongly acid solution the thiodydantoin ring is ruptured giving phenylalanine and substitution products. The absorption maxima of these dyes have also been determined and they are given in the tables at the end of the paper.

Experimental.

Thiohydantoin, prepared according to the method given in *Ber.*, 1898, **31**, 137, was condensed with aromatic aldehydes as follows: equimolecular proportions of the aldehydes and thiohydantoin were

heated together under reflux with 3-5 times the weight of acetic anhydride for periods varying from ½ to 3 hours. The solution was then poured into water, whereby the acetylated condensation product was precipitated in flocks which were collected, washed, dried and crystallised from various solvents, mostly from pyridine and glacial acetic acid, in glistening needles. Generally speaking these substances are sparingly soluble in most of the ordinary solvents and have got a remarkable power of crystallisation.

The deacetylation was effected by warming the above compounds with 20% solution of sodium hydroxide until completely dissolved and then precipitating the cooled solution with dilute hydrochloric acid. Then resulting products were then crystallised from glacial acetic acid or amyl alcohol in the form of silky needles which were dried at 120°. These deacetylated products are more soluble than the corresponding acetylated compounds in the ordinary organic solvents, and they have remarkable dyeing power for wool, silk and cotton. In caustic alkalis they are freely soluble. For the sake of abbreviation, the properties of all these compounds are given in tabular form at the end of the paper.

TABLE I.

Acetylated Compounds.

Name. (A = acetyl, T = thiohydantoin).	Appearance.	M. p.	Absorption maxima in glacial acetic acid (wave-lengths).	P. c. of sulphur (theoretical values in brackets.)
A-benzylidene-T.	Pale yellow needles	260°	4540	13·0 (13·0)
A-*o*-nitrobenzylidene-T.	Orange ,,	241°	5060	11·7 (11·5)
A-*m*-nitrobenzylidene-T.	Lemon-yellow ,,	263°	4930	11·2 (11·5)
A-*p*-nitrobenzylidene-T.	,, ,,	270°	4950	11·7(11·5)
Di-A-*o*-hydroxybenzylidene-T.	Deep yellow ,,	237°	4820	11·0 (10·5)
Di-A-*m*-hydroxybenzylidene-T.	,, ,,	250°	4710	10·9 (10·5)
Di-A-*p*-hydroxybenzylidene-T.	,, ,,	265°	4810	10·8 (10·5)
2 : 3-Thiocarbamidoquinoline-T.	Pale yellow prisms.	213°	——	15·6 (15·9)
Di-A-*m*-aminobenzylidene-T.	,, needles.	Above 285°	4710	10·7 (10·5)
Di-A-*p*-aminobenzylidene-T.	,, ,,	,, ,,	4750	10·9 (10·5)
Tri-A-3 : 5-dihydroxybenzylidene-T.	Orange yellow ,,	240°	4880	8·6 (8·8)
A-*p*-methoxybenzylidene-T.	Brownish-yellow needles.	265°	4720	11·4 (11·59)
A-3 : 4-methylenedioxybenzylidene-T.	,, ,,	275°	4790	11·6 (11·1)
Di-A-vanillidene-T.	Yellow needles.	261°	4800	9·9 (9·5)
A-cinnamylidene-T.	Deep yellow ,,	267°	4820	12·3 (11·8)
A-*p*-dimethylaminobenzylidene-T.	Bright red ,,	272°	5110	11·6 (11·1)

TABLE II.

Deacetylated Compounds.

Name. (T=thiohydantoin).	Appearance.	M. p.	Shade on wool and silk.	Absorption maxima in alcohol (wave-length.).	P. c. of sulphur (theoretical values in brackets.).
Benzylidene-T.	Pale yellow needles.	259°	Lemon yellow	4450	15·2 (15·5)
o-Nitrobenzylidene-T.	Orange yellow ,,	249°	Orange	4960	13·0 (12·85)
m-Nitrobenzylidene-T.	Pale yellow ,,	257°	Bright yellow	4860	13·1 (12·85)
p-Nitrobenzylidene-T.	,, ,,	266°	,, ,,	4910	13·2 (12·85)
o-Hydroxybenzylidene-T.	,, ,,	231°	,, ,,	4740	13·9 (14·5)
m-Hydroxybenzylidene-T.	,, ,,	256°	,, ,,	4680	14·5 (14·5)
p-Hydroxybenzylidene-T.	,, ,,	270°	,, ,,	4730	14·1 (14·5)
m-Aminobenzylidene-T.	,, ,,	Above 285°	,, ,,	4670	14·3 (14·5)
p-Aminobenzylidene-T.	,, ,,	,,	,, ,,	4710	14·2 (14·5)
3 :5-Dihydroxybenzylidene-T.	Bright yellow ,,	210°	Brownish-yellow	4760	13·9 (13·6)
p-Methoxybenzylidene-T.	,, ,,	255°	Canary ,,	4680	13·6 (13·65)
3 :4-Methylenedioxybenzylidene-T.	,, ,,	283°	Deep ,,	4740	12·9 (12·9)
Vanillidene-T.	,, ,,	240°	,, ,,	4750	13·9 (13·8)
Cinnamylidene-T.	,, ,,	260°	,, ,,	4760	13·5 (13·9)
p-Dimethylaminobenzylidene-T.	Light red ,,	252°	Orange-red	4980	12·4 (12·9)

CHEMICAL LABORATORY, ALLAHABAD UNIVERSITY.

Received March 27, 1930.

Reactivity of the Methylene Group in Coumarin-4-acetic Acids. Part III. Condensation of 7-Methylcoumarin-4-acetic Acid with *m*- and *p*-Hydroxybenzaldehydes.

By Biman Bihari Dey and Tiruvenkata Rajendra Seshadri.

It has been shown (Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 107) that salicylaldehyde reacts with coumarin-4-acetic acids, and particularly readily with their ethyl esters, by Knoevenagel's method, forming 4:3′-dicoumaryls. Of other aromatic aldehydes, the condensation of vanillin which has already been reported (Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 277) gave a product exhibiting very peculiar colour changes in the presence of alkalis. In view of the remarkable properties possessed by this body, a closer study of its derivatives, and a comparison with compounds of analogous constitution derived from other hydroxyaldehydes seemed to be desirable so as to throw further light on the mechanism of these colour changes.

The methyl ether and the acetyl derivative of the condensation product from vanillin have now been prepared and examined in respect of their behaviour with alkalis. The acetyl compound is insoluble in cold potash but slowly dissolves on warming, due to hydrolysis, and the usual colour effects are reproduced. In case of the methyl ether, on the other hand, it is found that although boiling alkalis dissolve it, evidently by the opening of the pyrone ring, the colour phenomena have disappeared completely, thus lending further support to the view already expressed (*loc. cit.*) that the production of the deep red colour and its subsequent fading should be attributed to the formation, initially, of a molecule which is quinonoid in all its tautomeric forms, this being followed by the opening of the pyrone ring and a consequent return to the normal structure.

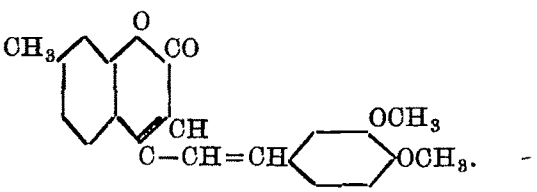
A study of properties of the compounds derived from *p*- and *m*-hydroxybenzaldehydes, which are described in this communication has also helped in confirming this hypothesis. The product from

p-hydroxybenzaldehyde possesses a close resemblance to the vanillin compound, the colour of the solid (golden yellow) and the changes it undergoes in solution in alkalis being identical in the two cases, while the *m*-hydroxy body is a colourless solid which dissolves in alkalis with only a faint yellow colour. This is in complete agreement with the expectation that an easy change into the quinonoid form would be possible only in the case of a molecule having a free hydroxyl in the *para*- and not in the *meta*-position

Coumarin-3-acetic acids, which have recently been synthesised in this laboratory, are being condensed with aromatic aldehydes, and it is hoped that the results would prove to be of interest in their bearing on this question.

Experimental.

7-Methyl-4-coumaryl-3′:4′-dimethoxyphenylethylene,



It was prepared from the vanillin compound (*J. Indian Chem. Soc.*, 1924, 1, 282), by methylation with methyl sulphate and sodium hydroxide. It crystallised from glacial acetic acid in pale yellow laminae melting at 188°. It was insoluble in dilute aqueous potash but dissolved slowly on boiling to a clear solution of a faint yellow colour. On acidification the unchanged methyl ether was deposited in the crystalline form.

7-Methyl-4-coumaryl-3′-methoxy-4′-acetoxyphenylethylene.

This was obtained in the usual way from acetic anhydride and a drop of pyridine. It was deposited from glacial acetic acid in colourless rectangular plates melting at 172°. When suspended in dilute sodium hydroxide, it remained unchanged for some minutes but slowly, and more rapidly on warming, the solid dissolved and the solution developed the characteristic red colour. Acids precipitated the original compound derived from vanillin, showing that hydrolysis had taken place.

7-Methyl-4-coumaryl-4′-hydroxyphenylethylene.

The condensation of *p*-hydroxybenzaldehyde with 7-methyl-coumarin-4-acetic acid was effected in the same way as with

vanillin, using Knoevenagel's method (*loc. cit.*). The crude product dissolved readily in a small volume of alcohol, and on allowing the solution to stand for a few hours, most of it separated out. It was further purified by solution in warm sodium hydroxide, precipitation with hydrochloric acid, and a final crystallisation from alcohol which yielded golden yellow plates melting at 218°. The colour reactions with aqueous alkalis and with concentrated sulphuric acid were found to be identical with those of the vanillin product. (Found: C, 76·9; H, 5·1. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0 per cent.).

The *methyl ether* crystallises from alcohol in fine pale yellow needles, melting at 180°. It dissolved only on boiling for some time with aqueous potash, and when the nearly colourless solution was acidified in the cold, the original methyl ether was slowly reprecipitated (m.p. 180°).

The *acetyl derivative* comes down from dilute acetic acid in colourless needles melting at 209° and slowly dissolves on leaving in contact with cold alkalis. Acidification regenerated the hydroxyphenylethylene (m.p. 218°).

7-Methyl-4-coumaryl-3′-hydroxyphenylethylene.

This product was obtained in a low yield by condensing 7-methylcoumarin-4-acetic acid with *m*-hydroxybenzaldehyde in the usual manner. It crystallised best from glacial acetic acid in the form of colourless laminae melting at 207°. It dissolved in cold dilute alkalis with only a pale yellow colour which faded slowly on standing and quickly on warming. The original body was immediately reprecipitated from the yellow solution on the addition of acids, whereas with the colourless solution the process was observed to be much slower. (Found: C, 77·2; H, 5·3. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0 per cent.),

The *methyl ether* crystallised as colourless needles from alcohol (m.p. 146°).

The *acetyl derivative* came down from glacial acetic acid as colourless plates (m.p. 159°).

Both the methyl ether and the acetyl compound, like the corresponding compounds derived from the 4′-hydroxyphenylethylene, were only slowly affected by aqueous alkali.

THE PRESIDENCY COLLEGE, MADRAS.

Received March 23, 1931.

Complexes of Antimony Halides with Sulphonium Halides.

By Prafulla Chandra Ray, Nadiabehari Adhikari, and Amarendra Nath Ray.

In course of a recent investigation (Ray and Adhikari, *J. Indian Chem. Soc.*, 1930, 7, 297) the exact nature of the reaction between mercuric iodide, alkyl sulphide (or polysulphide) and alkyl iodide has been clearly interpreted. It has been shown that alkyl sulphide and alkyl iodide interact to form sulphonium iodide which then combines with murcuric iodide to form compounds of the type of $[R_3S]_2HgI_4$ and $[R_3S]HgI_3$ analogous to the complex compounds K_2HgI_4 and $KHgI_3$. In the case of the alkyl polysulphides the extra sulphur atoms are split off and a sulphonium iodide is formed which then combines with mercuric iodide. Consequently the same compound is obtained starting with a sulphide or the corresponding polysulphide. That these compounds are really complexes of the type K_2HgI_4 and $KHgI_3$ is borne out by their general chemical behaviour and also by conductivity data.

This led the authors to investigate whether halides of any other metal, which do not belong to the mercury group, react in a similar way with alkyl sulphides and alkyl halides. In the course of the present work, the reaction between antimony halides, alkyl sulphides and alkyl halides, has been studied. Antimony was chosen because of its feeble electropositive character so that it may readily function as a central atom in a complex compound. Moreover compounds of the type $SbX_3 \cdot MX$ or $SbX_3 \cdot 3MX$ (X = halogen, M = alkali metal or ammonium) are quite well-known and are usually represented as $M[SbX_4]$ and $M_3[SbX_6]$. As a result the following compounds have been prepared and studied:—

(1)	$SbI_3 \cdot Et_3SI$	or	$Et_3S \cdot SbI_4$
(2)	$SbI_3 \cdot Me_3SI$	or	$Me_3S \cdot SbI_4$
(3)	$SbBr_3 \cdot Et_3SBr$	or	$Et_3S \cdot SbBr_4$
(4)	$SbCl_3 \cdot Et_3SI$	or	$Et_3S \cdot SbCl_3I$
(5)	$SbCl_3 \cdot Me_3SI$	or	$Me_3S \cdot SbCl_3I$
(6)	$SbI_3 \cdot 3\{Et_3SBr\}$ $SbBr_3 \cdot 3\{Et_3SI\}$	or	$3Et_3S \cdot SbBr_3I_3$

The same compounds are obtained if we start with antimony halides and the corresponding sulphonium halide.

It has also been noticed that a sulphur atom is split off when a disulphide is substituted for the corresponding monosulphide resulting in the formation of an identical compound. All of these are coloured crystalline compounds, rather sparingly soluble in acetone, except the compound $[Et_3S]SbBr_4$ which freely dissolves, and is practically insoluble in other organic solvents. They are however decomposed by an excess of water, oxyhalides being precipitated.

Constitution.—These are undoubtedly complex compounds, although not of pronounced stability, of the type $MSbI_4$ or rather $[SbI_4]M$ according to Werner's method of formulation ionising in concentrated solution into the ions, SbI_4^- and M^+. A solution of these compounds in acetone is coloured and on adding water gradually the colour disappears. An oxyhalide is precipitated only when sufficient water is added after the colour is fully discharged. The disappearance of colour is obviously due to the collapse of the complex. The values obtained for molecular conductivity at varying dilutions indicate that the compound dissociates into two ions at lower dilution although at higher dilutions the conductivity increases, presumably due to the breaking down of the complex. The complex nature of the series of compounds is also indicated by the fact that identical compound is obtained when either (*i*) SbI_3 is treated with excess of Et_3SBr or (*ii*) $SbBr_3$ is treated with excess of Et_3SI. If these were mere additive compounds, we would have expected two different compounds namely (*i*) $SbI_3 \cdot 3Et_3SBr$ and (*i*) $SbBr_3 \cdot 3Et_3SI$. The identity of these two compounds, as indicated by their chemical and physical properties and also melting point, can only be satisfactorily explained by assuming that a complex compound of the type $[Et_3S]_3 \cdot [SbI_3Br_3]$ is formed. It has been shown previously (Atkinson, *Chem. News*, 1883, **47**, 175 ; *J. Chem. Soc.*, 1883, **43**, 291) that the compounds $3KBr \cdot SbCl_3$ and $3KCl \cdot SbBr_3$ are also identical and hence has been represented as $K_3[SbCl_3Br_3]$.

The constitution of the other compounds of the series should therefore be represented as of the type $[Et_3S]SbX_4$ (X = halogen).

Experimental.

Preparation of $[Et_3S]Sbl_4$.—Antimony tri-iodide, ethyl sulphide and ethyl iodide in molecular proportions are gently warmed together

on a water-bath under reflux. A mass of reddish-yellow powder is obtained which is separated and is purified by crystallisation from acetone. The compound is rather sparingly soluble and hence to bring it into solution, treatment with a large volume of boiling acetone is necessary. The bulk of the acetone is then removed by distilling gently from the water-bath. Crystals separate as the acetone is distilled off and on cooling further crystallisation occurs.

It is a red, glistening crystalline substance, m.p. 169°, sparingly soluble in acetone and insoluble in other solvents. It is decomposed on adding an excess of water. (Fonnd: Sb, 15·99, 16·28; I, 68·26, 68·36; C, 9·41. $(C_2H_5)_3SI \cdot SbI_3$ requires Sb, 16·26; I, 67·84; C, 9·61 per cent. Sulphur is found to be present qualitatively).

If SbI_3, Et_2S_2 and ethyl iodide, in equimolecular proportions, are heated together for about 2 hours under reflux, the contents of the flask gradually turn tarry. The tarry mass dissolves in acetone and on the addition of ether, a reddish-yellow substance is precipitated. This is separated and crystallised from acetone in the same way as the above compound. This has the same melting point (169°) and physical and chemical properties as the above compound. (Found: Sb, 16·15 per cent.).

The same compound is also obtained by treating antimony tri-iodide with $(C_2H_5)_3SI$. The compound $SbI_3 \cdot 3Et_3SI$ however could not be obtained, as might be expected, on treating SbI_3 with an excess of Et_3SI.

Preparation of $[Me_3S]SbI_4$.—It was prepared exactly in the same way as $[Et_3S]SbI_4$ from antimony iodide, methyl iodide and dimethyl sulphide. It is a reddish-yellow compound, m.p. 194°. Its properties are very similar to those of $[Et_3S]SbI_4$. (Found: Sb, 17·16; I, 72·43. $[(CH_3)_3S]SbI_4$ requires Sb, 17·28; I, 71·87 per cent.).

Sulphur was found to be present qualitatively. The same compound results when SbI_3 is either heated with $(CH_3)_2S_2$ and CH_3I or with $(CH_3)_3SI$. The compound $SbI_3.3[(CH_3)_3SI]$ could not be prepared.

Preparation of $[Et_3S]SbBr_4$.—Antimony tribromide, diethly sulphide and ethyl bromide in equimolecular proportion were heated on the water-bath, under reflux. The product, a heavy liquid, readily dissolved in acetone but no precipitate was obtained on adding ether. The acetone was evaporated off and a greenish mass was left behind. It was redissolved in acetone and crystallised,

It is a greenish compound, melting at 68°. It freely dissolves in acetone. On adding water decomposition takes place. (Found: Sb, 21·47; Br, 57·16. $[(C_2H_5)_3S]SbBr_4$ requires Sb, 21·36; Br, 57·03 per cent. Sulphur was found to be present qualitatively.)

Preparation of $[Et_3S]SbCl_3I$.—Antimony trichloride, ethyl sulphide and ethyl iodide in equimolecular proportion were gently warmed on the water-bath for a few minutes. The product of reaction, a viscous mass, was dissolved in acetone and precipitated by ether. The precipitate was dissolved in boiling acetone and crystallised in the usual way. It is a yellow shining crystalline substance, m.p. 156°. It is rather sparingly soluble in acetone and insoluble in other organic solvents. It is decomposed on adding excess of water. (Found: Sb, 25·71; Cl, 22·43, 22·41; I, 26·56; C, 14·92. $[(C_2H_5)_3S]SbCl_3I$ requires Sb, 25·68 ; Cl, 22·45 ; I, 26·79; C, 15·18 per cent.). When the reactants were heated for 2 to 3 hours, the whole mass turned tarry black. The tarry mass was dissolved in acetone and on the addition of ether, a yellow substance was precipitated. The precipitate was separated, dissolved in boiling acetone and an yellow crystalline substance was isolated in the usual way. It has the same melting point (156°) as the compound $[(C_2H_5)S]\cdot SbCl_3I$ and also identical physical and chemical properties. (Found: Sb, 25·88 per cent.).

The same compound was also obtained when $SbCl_3$ was treated with $(C_2H_5)_3SI$.

Preparation of $[Me_3S]SbCl_3I$.—Antimony trichloride, methyl sulphide and methyl iodide in about equimolecular proportions were warmed on the water-bath with a little acetone. Brilliant yellow crystals separated. These were separated and recrystallised from acetone in the usual way. It is a yellow crystalline substance, m.p. 189°. It is sparingly soluble in acetone. Its chemical properties are very similar to those of $[C_3H_5)_3S]SbCl_3I$. (Found: Sb, 27·98; Cl, 24·57; C, 29·22. $[(CH_3)_3]SbCl_3I$ requires Sb, 28·17; Cl, 24·63; C, 29·48 per cent.).

Preparation of $[Et_3S]_3SbBr_3I_3$.—Antimony tri-iodide was treated with ethyl sulphonium bromide in a large volume of acetone. A yellowish-red substance gradually separated but the contents were then warmed a little to ensure complete reaction. The precipitate was separated and crystallised from acetone.

It is a reddish-yellow substance, m.p. 182 83°. It is sparingly soluble in acetone and insoluble in other organic solvents. The

properties are similar to other compounds of the series. (Found: Sb, 10·93; total halide as AgBr and AgI, 0·2207 gm. from 0·2240 gm. of the substance. $[(C_2H_5)_3S]_3SbBr_3I_3$ requires Sb, 11·08; total halide, 0·2176 gm.

Conductivity of $[Et_3S]SbI_4$ *in acetone at* 27°.

Dilution (in litres).	Molecular conductivity.
570	126·7
1140	159·3
2280	205·6
4560	243·3
9120	279·8
18249	350·3

UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA.

Received March 18, 1931.

Some New Hydrocupreidine Derivatives. Part I.

By Sudhamoy Ghosh and Nihar Ranjan Chatterjee.

The alkyl ethers of hydrocupreine, like ethyl-, *iso*propyl-, *iso*amyl-, and *iso*-octyl derivatives have been all synthesised (Heidelberger and Jacobs, *J. Amer. Chem. Soc.*, 1922, **44**, 1091; Giemsa and Halberkann, *Ber.*, 1918, **51**, 1825) and found to possess marked bactericidal or local anaesthetic properties. The study of the hydrocupreidine derivatives appears, however, to have been limited only to the ethyl derivative and we thought it desirable to synthesise them for a similar study. As the *iso*alkyl derivatives of hydrocupreine are known to be more active than the normal compounds we took up the preparation of the *iso*-series of the hydrocupreidines first. The preparation of the normal series is also nearing completion.

The starting material in our preparations was hydroquinidine which was demethylated to hydrocupreidine by boiling with hydrobromic acid (Heidelberger and Jacobs, *J. Amer. Chem. Soc.*, 1919, **41**, 817). The OH-group thus set free was then alkylated. Heidelberger and Jacobs prepared the ethyl hydrocupreidine by the process outlined in D. R. P. 254712 applied in the case of hydrocupreine derivatives and mentioned below as "cold process." We first prepared the *iso*propyl-, *iso*butyl-, *iso*amyl- and secondary octyl hydrocupreidine by the cold process but as it took a long time to complete and the yield was low we modified it by warming with a catalyst as described below. The yield was increased and there was considerable economy of time.

Experimental.

iso*Propylhydrocupreidine*, $C_{22}H_{30}O_2N_2$.

(*a*) *By Cold Process.*—The hydrocupreidine (3 g.) was dissolved in a little absolute alcohol and treated with the calculated quantity of 50 % potassium hydroxide. The mixture was warmed on the water-bath until clear, cooled in an ice-chest and then treated with *iso*propyl iodide. The solution was allowed to stand at room

temperature for a month and then chilled to 0° and filtered from potassium iodide. The filtrate was acidified with dilute hydrochloric acid and extracted with ether. The aqueous liquid was then made strongly alkaline with caustic soda and shaken with ether. The ethereal solution was washed with water and evaporated. The *iso*propylhydrocupreidine thus obtained was recrystallised from 50 % alcohol (yield, 2·02 g.).

(*b*) *By Modified Process.*—The hydrocupreidine (6 g.) was dissolved in absolute alcohol and treated with the calculated quantity of 50 % potassium hydroxide. It was warmed on the water-bath until clear, cooled and treated with *iso*propyl iodide and freshly prepared copper paste obtained from one gram of copper sulphat. The mixture was boiled on the water-bath under reflux for abouet 8 hours and the product poured into dilute hydrochloric acid. It was then shaken with ether, the aqueous liquid filtered, made strongly alkaline with caustic soda and the base extracted with ether. The ethereal liquid was washed, shaken with dilute hydrochloric acid and precipitated with sodium hydroxide. It was then recrystallised from 50 % alcohol (yield 4·4 g.).

The base crystallised from alcohol in colourless needles, m.p. 181°. It was readily soluble in alcohol, chloroform and ether but insoluble in water. It gave a beautiful blue fluorescence with dilute sulphuric acid. $[\alpha]_D^{30°} = +206·25°$ ($c=2$, in absolute alcohol). (Found: N, 7·69. $C_{22}H_{30}O_2N_2$ requires N, 7·90 per cent.).

iso*Propylhydrocupreidine Hydrochloride*, $C_{22}H_{30}O_2N_2$, 2HCl.—It was prepared by treating the base with dilute hydrochloric acid in aqueous suspension and recrystallised from alcohol. It formed colourless plates, melting at 249° to a brown liquid. It was soluble in water and alcohol. $[\alpha]_D^{30°} = +260°$ ($c=1$, in $N/10$-hydrochloric acid. (Found: Cl, 16·21. $C_{22}H_{30}O_2N_2$, 2HCl requires Cl, 16·60 per cent.).

iso*Butylhydrocupreidine*, $C_{23}H_{32}O_2N_2$.—By the cold process 5·2 g. of hydrocupreidine gave 1·5 g. of the base and by the hot process 10·4 g. gave 4·65 g. The base could not be crystallised tion from ordinary solvents and it was purified by repeated precipitafrom the acid solutions. (Found: N, 7·13. $C_{23}H_{32}O_2N_2$ requires N, 7·60 per cent.).

iso*Butylhydrocupreidine Hydrochloride*, $C_{23}H_{32}O_2N_2$, 2HCl.—It was obtained in the usual way and slowly crystallised in *vacuo* in

long colourless needles. It was freely soluble in water and alcohol and partially so in chloroform. It melted at 211° to a dark liquid with previous blackening. $[\alpha]_D^{23} = +212°$ ($c=1$, in water). (Found: Cl, 15·81; N, 5·96. $C_{23}H_{32}O_2N_2$, 2HCl requires Cl, 16·08 N, 6·35 per cent.).

iso*Amylhydrocupreidine*, $C_{24}H_{34}O_2N_2$.—6·2 G. of hydrocupreidine gave 1 g. of the base by the cold process and 9 g. gave 4·7 g. of the base by the hot process. It crystallised from 50 % alcohol in tufts of colourless needless, m.p. 168°. It was soluble in absolute alcohol, ether, chloroform and benzene. It gave a beautiful fluorescence with dilute sulphuric acid. $[\alpha]_D^{30} = +204°$ ($c=2$, in absolute alcohol). (Found: N, 7·15. $C_{24}H_{34}N_2O_2$ requires N, 7·33 per cent.).

iso*Amylhydrocupreidine Hydrochloride*, $C_{24}H_{34}O_2N_2$, 2HCl.—It was prepared in the usual way and recrystallised from dilute alcohol in microscopic needles, m.p. 229° (decomp). $[\alpha]_D^{23} = +215°$ ($c=1$, in water). (Found: Cl, 15·45. $C_{24}H_{34}O_2N_2$, 2HCl requires Cl, 15·58 per cent.).

Secondary Octylhydrocupreidine Hydrochloride, $C_{27}H_{40}O_2N_2$, 2HCl.—9 G. of hydrocupreidine gave only 0·5 g. of the base by the cold process and 9 g. gave 1·5 g. of the base by the hot process. It could not be crystallised from the usual solvents. The hydrochloride crystallised from hot water in colourless needles, m.p. 227° (decomp.). It was soluble in hot water and alcohol and partially so in chloroform and benzene. It was less soluble in cold water and acetone. $[\alpha]^{32} = +197·0°$ ($c=1$, in $N/25$-hydrochloric acid). (Found: Cl, 13·93; N, 5·13. $C_{27}H_{40}O_2N_2$, 2HCl requires Cl, 14·15; N, 5·59 per cent.).

Summary.

1. The preparation of some new hydrocupreidine derivatives, *iso*propyl-, *iso*butyl-, *iso*amyl- and sec.-octylhydrocupreidines, are described, the corresponding isomeric hydrocupreines being all physiologically active.

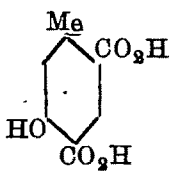
2. The 'cold process' for the preparation of alkyl hydrocupreines was found to be tedious, uneconomical and unsatisfactory regarding yield, when applied to hydrocupreidines. The method has been improved upon.

The Condensation of Chloral with *m*-Cresotic Acid.

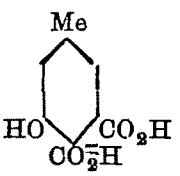
By Narshinh Muljibhai Shah and Rupchand Lilaram Alimchandani.

The condensation of chloral (*a*) with *m*-cresotic acid has been studied by Alimchandani and Meldrum (*J. Chem. Soc.*, 1921, **119**, 201; *J. Indian Chem. Soc.*, 1925, **2**, 1) and by Schleussner and Voswinckel (*Annalen*, 1921, **422**, 111); (*b*) with the methyl ether of *m*-cresotic acid by Meldrum and Alimchandani (*J. Indian Chem. Soc.*, 1929, **6**, 253).

The condensation product, when *m*-cresotic acid is used, is a complex mixture. Hence Meldrum and Alimchandani attempted to simplify matters by working with the methyl ether of the acid. The result was the production of evidence that chloral condenses with the benzene nucleus in the *para*-position to the methoxy group: α-coccinic acid (V) was obtained from its methyl ether as the ultimate product.



α-Coccinic acid.



γ-Coccinic acid.

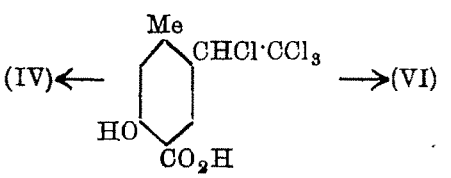
Schleussner and Voswinckel found that chloral condenses with *m*-cresotic acid in the *meta*-position to the hydroxy group: they obtained, as ultimate products, γ-coccinic acid and its methyl ether, the latter agreeing in melting point with the methyl ether obtained by Meldrum (*J. Chem. Soc.*, 1911, **99**, 1712).

We have made an intensive study of the condensation of chloral with *m*-cresotic acid, with a view to ascertain the structure of the different products. We find that chloral condenses in the *para*-position to the hydroxy group as Meldrum and Alimchandani found with the methyl ether.

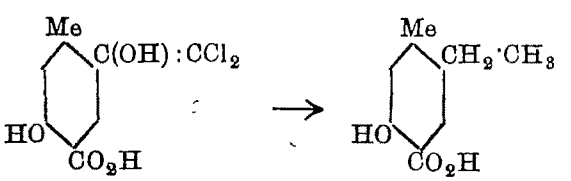
It has been possible to isolate three crystalline substances from the condensation product of chloral with *m*-cresotic acid: (*a*) 4-hydroxy-5-carboxy-2-methyl-1-α-hydroxy-βββ-trichloroethylbenzene(I), (*b*) the lactone of that substance (II), and (*c*) 4-hydroxy-5-carboxy-2-methyl-α-hydroxy-ωω-dichlorostyrene (III).

The question had to be settled where the linking of the chloral molecule takes place. The substance (I) on hydrolysis yielded a substituted mandelic acid (IV) which on oxidation gave α-coccinic acid (V) identical with that obtained by Meldrum and Alimchandani on hydrolysis of the methyl ether (1929, *loc. cit.*). The same acid was obtained directly by the oxidation of the substance (I).

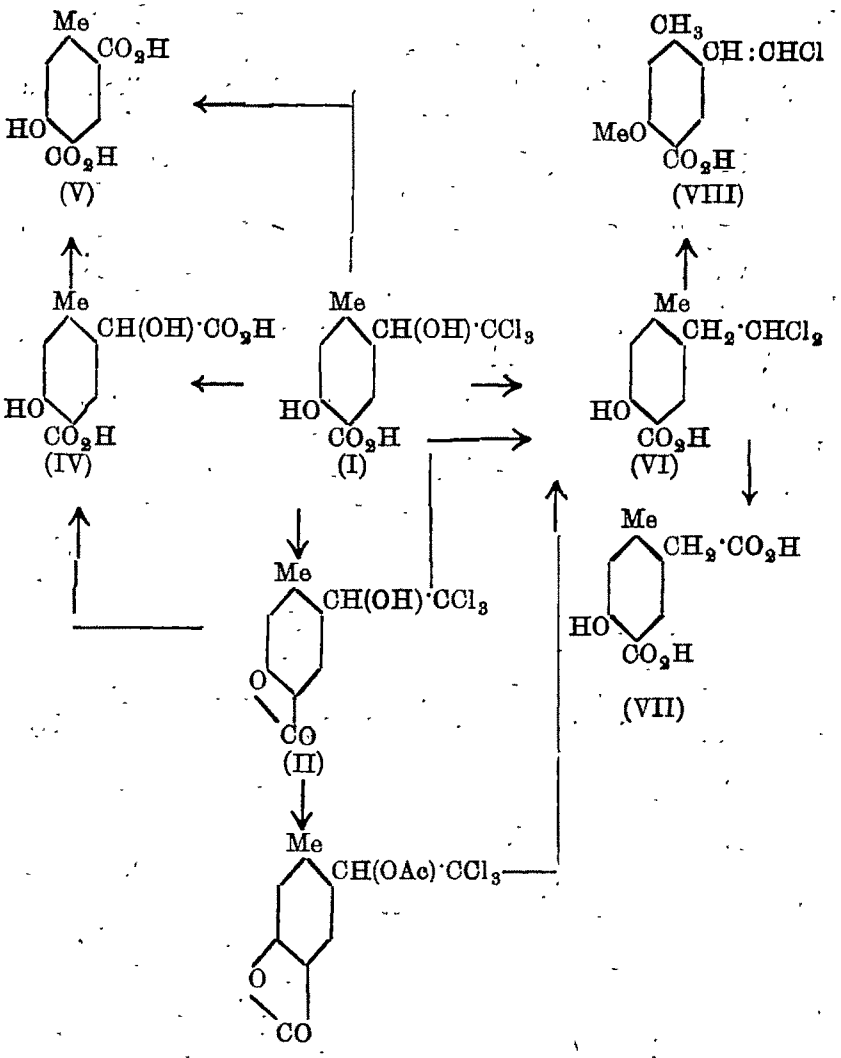
Further, the substance (I) on reduction with zinc and acetic acid gave 2-methyl-5-carboxy-4-hydroxy-1-ββ-dichloroethylbenzene (VI), which on methylation was found to be identical with that of Meldrum and Alimchandani (1929, *loc. cit.*). The substance (VI) on treatment with sulphuric acid gave a phenylacetic acid (VII) which on methylation yielded the methyl ether of the phenylacetic acid identical with that of Meldrum and Alimchandani. The methyl derivative of the substance (VI) on treatment with sodium hydroxide gave the substance (VIII).



(X)



(III) (IX)



The substance (II) gives the same products as (I) on similar treatment: (*a*) the mandelic acid (IV) on hydrolysis, and (*b*) the product (VI) on reduction. The amount of the substance (II) obtained from the condensation mixture is small. It was found possible to prepare it in quantity from the substance (I) by heating at its melting point.

The formula (II) which is that of a β-lactone, may seem unlikely. However, any formula other than (II) for this lactone is excluded because the substance (*i*) does not give ferric chloride reation, (*ii*) dissolves slowly in hot sodium hydroxide and (*iii*) gives a monoacetyl.

derivative, which on reduction with zinc and acetic acid gives the product (VI) with elimination of the acetyl group.

The formation of the substance (III) depends on the elimination of a molecule of hydrochloric acid from the substance (I) (*cf.* Chattaway and Prats, *J. Chem. Soc.*, 1927, p. 685). The substance (III) on reduction gave the substance (IX) *i.e.*, $-C(OH):CCl_2$ was changed into $-CH_2 \cdot CH_3$. On acetylation, the substance (III) gave a diacetyl derivative. All attempts to prepare a semicarbazide and a phenylhydrazone or an osazone were fruitless. Hence it tends to react mainly in the enolic form. Chattaway and Prats (*loc. cit.*) found that their substance showed keto-enolic isomerism.

All our condensation products contain the chloral molecule in the *para*-position to the hydroxyl group. Schleussner and Voswinckel (*loc. cit.*) found that condensation of chloral with *m*-cresotic acid takes place in the *meta*-position. In order to ascertain whether this difference is due to a difference in the concentration of the condensing agent (sulphuric acid) or to the higher temperature at which the reaction was carried out in India, or to both these causes, the condensation was tried under varying conditions:—

(*a*) Schleussner and Voswinckel's condensation was repeated by keeping the condensing mixture (*i*) for 24 hours and (*ii*) for 8 days in a refrigerator.

(*b*) The experiment was repeated, the condensing agent being 90 per cent. sulphuric acid.

In all cases, hydrolysis and oxidation of the condensation product led not to γ-coccinic acid but to α-coccinic acid.

Generally the indications are that the substances with which Schleussner and Voswinckel worked were not pure. This is due first to the fact that the complex condensation mixture is difficult to crystallise and second to the fact that instead of crystallising from an organic solvent, they treated the product by dissolving in dilute alkali and acidifying with hydrochloric acid. The resulting precipitate was then washed and dried at 105°, when it lost water and melted at about 300°. Their substance of the same empirical composition as (IV) is described by them as yellowish, m.p. 204°. The authors find that their crude substance is yellowish, m.p. 211-12°, and on purification by means of its barium salt becomes white, m.p. 227°.

Chattaway and Calvet (*J. Chem. Soc.*, 1928, p. 2914) have obtained from chloral and *p*-nitroanisol, as the sole product of reaction, a substance which contains the group $-CHCl \cdot CCl_3$. Meldrum and

Alimchandani (*loc. cit.*) also got a substance with the same group in the condensation of the methyl ether of *m*-cresotic acid. A substance (X) containing the same group is obtained when hydrochloric acid gas is passed into the mixture of chloral, *m*-cresotic acid and sulphuric acid. For some purposes, the groups $-CHCl\cdot CCl_3$ and $-CH(OH)\cdot CCl_3$ are equivalent. The substance (X), on hydrolysis and on reduction gave respectively the products (IV) and (VI), which are got on similar treatment of the substance (I) containing the group $-CH(OH)\cdot CCl_3$.

Experimental.

4-Hydroxy-5-carboxy-2-methyl-1-α-hydroxy-βββ-trichloroethylbenzene (I)—*m*-Cresotic acid (10 g.), chloral hydrate (11 g.) and sulphuric acid (97·98 per cent, 50 c.c.) were mixed and the materials formed a clear solution on shaking. On the third day, the mixture was poured over ice; a solid separated which was collected, washed with hot water and dried in an air-oven at 90° (yield, 12 g.). The crude product (A) was worked up separately (see below).

The filtrate was evaporated on the hot air-bath when needle-shaped crystals of the substance (I) were obtained (4 g.) which were found to effloresce. It was crystallised from a mixture of methyl alcohol and benzene as rhombic plates, m.p. 218° with effervescence. (Found: Cl, 35·54. $C_{10}H_9O_4Cl_3$ requires Cl, 35·53 per cent.).

It is soluble in acetic acid, acetone, alcohols and ether, insoluble in benzene, toluene and petrol. The alcoholic solution of the substance gave an intense violet coloration with ferric chloride.

The *acetyl* derivative, prepared in the usual manner, was crystallised from benzene, m.p. 160°. (Found: Cl, 27·92. $C_{14}H_{13}O_6Cl_3$ requires Cl, 27·74 per cent.).

The sulphuric acid mother-liquor, when evaporated further and cooled, deposited long silky crystals of sulpho-*m*-cresotic acid.

Lactone of 4-Hydroxy-5-carboxy-2-methyl-1-α-hydroxy-βββ-trichloroethylbenzene (II) *and 4-Hydroxy-5-carboxy-2-methyl-α-hydroxy-ωω-dichlorostyrene* (III).—The crude product (A) was dissolved in glacial acetic acid. The solution deposited on keeping for a day a small quantity of the substance (II). The mother-liquor (B) was worked up separately (see below). The substance (II) was first crystallised from a mixture of ether and petrol and then for

analysis from acetone as lustrous plates, m.p. 340° (decomp). (Found: Cl, 37·77. $C_{10}H_7O_3Cl_3$ requires Cl, 37·80 per cent.). The substance does not give a violet coloration with ferric chloride. It is soluble in ether, sparingly soluble in glacial acetic acid, acetone and insoluble in petrol.

The substance (II) was prepared in quantity thus:—

The substance (I), m.p. 218° (5 g.), was heated in a sulphuric acid bath at about 220-23°. When the effervescence was over, the fused mass was cooled and heated with glacial acetic acid, when a white crystalline powder was obtained. Recrystallised from acetone; m.p. 340° (decomp.).

The *acetyl* derivative, prepared in the usual manner, crystallised from ethyl acetate, m.p. 315°. (Found: Cl, 32·86. $C_{12}H_9O_4Cl_3$ requires Cl, 32·91 per cent.).

The acetic acid mother-liquor (B) was diluted with water till a white turbidity was obtained which dissolved on heating. On cooling a non-crystallisable mass separated as an oil which solidified on keeping. Schleussner and Voswinckel (*loc. cit.*) also found that an oily substance of varying composition was obtained on dilution with water.

The filtrate on further diluting with water deposited a light powder (III). It was crystallised from a mixture of ether and petrol and then from methyl alcohol for analysis, m.p. 165° (decomp.). (Found: Cl, 27·08. $C_{10}H_8O_4Cl_2$ requires Cl, 26·96 per cent.). It is soluble in acetic acid, acetone, ether, alcohols; insoluble in petrol and benzene. The alcoholic solution gave a violet coloration with ferric chloride.

The *acetyl* derivative was crystallised from chloroform, m.p. 216-17° (decomp.). (Found: Cl, 20·48. $C_{14}H_{12}O_6Cl_2$ requires Cl, 20·46 per cent.).

The remaining mother-liquor on evaporation to a small bulk, yielded a small quantity of the substance (I).

4-Hydroxy-5-carboxy-2-methylmandelic Acid (IV).—The trichloroethylbenzene (I), m.p. 218° (10 g.), was heated on a water-bath with sodium hydroxide (200 c.c. of 10 per cent.) for three hours. A yellowish solution was obtained which was filtered and acidified with dilute sulphuric acid. The filtrate on keeping deposited clusters of yellowish prismatic needles, m.p. 211-12°. The crude acid was purified through its barium salt. The salt was dissolved in water and treated with dilute sulphuric acid. Barium sulphate was

removed and the filtrate gave prismatic crystals, m.p. 227° (efferv.). (Found: equivalent, 113·9 ; C, 52·97 ; H, 4·45. $C_{10}H_{10}O_6$ requires equivalent, 113·04 ; C, 53·10 ; H, 4·43 per cent.). The *barium* salt crystallises with 4 molecules of water, of which 2 molecules are removed by heating at 115-20°. (Two samples were analysed; Found: Ba, 31·77, 31·74. $C_{10}H_8O_6Ba$, $4H_2O$ requires Ba, 31·71 per cent. After heating to constant weight at 115-20°, found: Ba, 33·93, 34·12. $C_{10}H_8O_6Ba$, $2H_2O$ requires Ba, 34·58 per cent.).

The *acetyl* derivative was prepared in the usual way ; it was crystallised from water, m.p. 168-70° (efferv.). It crystallises with 1 molecule of water. (The *hydrated* substance, found: equivalent 164·3 ; H_2O, 5·46. $C_{14}H_{14}O_8$, H_2O requires equivalent, 164·05 ; H_2O, 5·49 per cent. The *anhydrous* substance, found: equivalent, 154·09. $C_{14}H_{14}O_8$ requires equivalent, 155·05).

The substance (II) on hydrolysing with sodium hydroxide gave the above mandelic acid :—The substance (II, 2 g.) was mixed with sodium hydroxide (60 c.c. of 10 per cent.); it slowly dissolved when heated on the water-bath. The solution was further heated for about three hours, filtered, and acidified with hydrochloric acid when a yellowish crystalline powder separated. The acid was purified by preparing its barium salt. The mixed melting point of the acid with the mandelic acid described above was 227° (efferv.).

α-Coccinic Acid (V).—The mandelic acid (IV, 1 g.) was dissolved in just sufficient potassium hydroxide solution (20 per cent.). Potassium permanganate (1 g. in 80 c.c. water) solution was added slowly. The mixture was heated for half an hour on the water-bath. The precipitated manganese oxide was filtered off ; the filtrate was concentrated and acidified. The acid came down as a white precipitate which was crystallised from glacial acetic acid, m.p. 316-18° (decomp.). The mixed melting point with Meldrum and Alimchandani's α-coccinic acid was 318°.

The same acid was also obtained by the oxidation of the substance (I). The substance (1 g.) was dissolved in sodium hydroxide (20 c.c. of 10 per cent.) and heated on a water-bath for about 8 hours after which more sodium hydroxide (15 c.c.) was added. Potassium permanganate (0·75 g. in 25 c.c. water) was added slowly and the mixture heated on the water-bath for about two hours. After the removal of manganese oxide, the filtrate was reduced to a small bulk and acidified. The substance on crystallisation was found to be identical with the α-coccinic acid already obtained.

2-Methyl-5-carboxy-4-hydroxy-1-ββ-dichloroethylbenzene (VI).—To the hot solution of the substance (I, 10 g.) in acetic acid (40 c.c.), zinc dust (4-5 g.) was added little by little ; the mixture was boiled slightly. After the reaction was over, the mixture was filtered and filtrate diluted with water, when a white light substance separated. It was first crystallised from acetic acid and then from dilute ethyl alcohol ; soft silky needles, m. p. 206.° (Found: Cl, 28·51. $C_{10}H_{10}O_3Cl_2$ requires Cl, 28·47per cent.).

The same substance was obtained from the substance (II) by subjecting it to reduction with zinc and acetic acid. The substance (II) was suspended in hot glacial acetic acid. On adding zinc dust, as the reaction proceeded, it dissolved. As before, the reduction product was obtained by adding water to the filtrate. The product on crystallisation was found to be identical with the reduction product described above.

Further, the acetyl derivative of the substance (II) was similarly reduced by means of zinc and acetic acid. The reduction product was found to be identical with (VI).

The *acetyl* derivative was crystallised from benzene, m.p. 170°. (Found: Cl, 24·04. $C_{12}H_{12}O_4Cl_2$ requires Cl, 24·37 per cent.).

The *methyl* derivative was prepared in the usual way by means of dimethyl sulphate. During the course of methylation, the temperature was not allowed to rise above 45°. The methylated product was found to be identical in every respect with that of Meldrum and Alimchandani (*loc. cit.*).

4-Hydroxy-5-carboxy-2-methylphenylacetic Acid (VII).—The dichloroethylbenzene (VI, 5 g.) was heated with conc. sulphuric acid (50 c.c.) on a water-bath when hydrochloric acid was evolved. After the reaction was over, the cooled mixture was poured into water, when a white substance separated. The crude acid was purified by preparing its barium salt which on acidifying with hydrochloric acid gave the phenylacetic acid as needles. It was crystallised from water in which it is sparingly soluble, m.p. 251°. (Found: equivalent, 105·7. $C_{10}H_{10}O_5$ requires equivalent, 105·04).

The *barium* salt crystallises with 2 molecules of water, of which one is removed by heating at 115-20°. (Found: Ba, 35·96. $C_{10}H_8O_5Ba, 2H_2O$ requires Ba, 36·02 per cent. after heating to constant weight at 115-120°, found: Ba, 37·75. $C_{10}H_8O_5Ba, 1H_2O$ requires Ba, 37·81 per cent.).

The *methyl* derivative was prepared in the usual manner by means of dimethyl sulphate and was found to be identical with that of Meldrum and Alimchandani (*loc. cit.*).

4-Methoxy-5-carboxy-2-methyl-ω-chlorostyrene (VIII).—If the temperature is allowed to rise during the methylation of the substance (VI), a white powder begins to separate. It was found to be a sodium salt, which on acidifying gave the substance (VIII). It was crystallised from glacial acetic acid as double pyramids, m.p. 163°. (Found: Cl, 15·71. $C_{11}H_{11}O_3Cl$ requires Cl, 15·65 per cent.). The substance did not give a violet coloration with ferric chloride.

The same substance was prepared from the methyl derivative of the substance (VI). The derivative (1 g.) was dissolved in sodium hydroxide (20 c.c. of 20 per cent.). On heating, the sparingly soluble sodium salt began to separate, which on acidification yielded the substance, m.p. 168°.

4-Hydroxy-5-carboxy-2-methyl-1-ethylbenzene (IX).—To the hot solution of the substance (III) in acetic acid, zinc dust was added in small quantity at a time. Vigorous reaction took place. The mixture was boiled, filtered and the filtrate diluted with water. The reduction product was crystallised from methyl alcohol, m.p. 315° (decomp.). (Found: equivalent, 180·0; C, 66·08; H, 6·83. $C_{10}H_{12}O_3$ requires equivalent, 180·1; C, 66·63; H, 6·72 per cent.).

4-Hydroxy-5-carboxy-2-methyl-1-αβββ-tetrachloroethylbenzene (X).—*m*-Cresotic acid (15 g.), chloral hydrate (27 g.) and sulphuric acid (120 c.c.) were mixed together. Dry hydrochloric acid gas was passed into the solution for about 8 hours. On the third day, the mixture was poured over ice. A white precipitate was obtained, which was dried and dissolved in glacial acetic acid: rectangular plates, recrystallised from benzene, m.p. 227-28° (efferv.). (Found: Cl, 44·20. $C_{10}H_8O_3Cl_4$ requires Cl, 44·60 per cent.).

The *acetyl* derivative was crystallised from toluene and then from alcohol, m.p. 197°. (Found: Cl, 39·32. $C_{12}H_{10}O_4Cl_4$ requires Cl, 39·40 per cent.)

The substance (X, 5 g.) was boiled for an hour with potassium hydroxide (100 c.c. of 20 per cent.). On acidifying the solution, a small quantity of a dark substance separated, which was removed; the filtrate deposited a crystalline powder, which was purified by preparing its barium salt. After removing barium as barium sul-

phate, the acid obtained was found to be identical with the mandelic acid obtained by the hydrolysis of the substance (I).

The tetrachloroethylbenzene (X) was reduced by means of zinc and acetic acid as before. The reduction product was similarly obtained and found to be identical with that got by the reduction of the substance (I).

In conclusion, the authors wish to express their gratitude to Dr. A. N. Meldrum for his kind encouragement throughout the course of this work; part of the work was carried out with his permission at the Royal Institute of Science, Bombay. The authors also wish to thank the University of Bombay for a grant to one of them (R.L.A.) in aid of this investigation.

KARNATAK COLLEGE,
DHARWAR.

Received February 28, 1931.

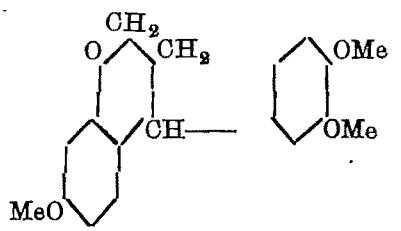
On Some Derivatives of 4-Phenylchroman.

By Prafulla Chandra Mitter and Prafulla Kumar Paul.

In order to study the properties of hydroxylated 4-phenylchromans which are of interest in their bearing on brazilin derivatives and their syntheses, it was considered desirable to prepare in the first place 7-methoxy-4-phenylchroman.

Our original plan was to prepare 2:4-dimethoxy-$\beta\beta$-diphenylacrylic acid and to reduce it to the corresponding propionic acid and then over the ester to 2:4-dimethoxy-$\beta\beta$-diphenylpropyl alcohol, the alcohol being converted subsequently into 7-methoxy-4-phenylchroman. It was found convenient to start with 7-methoxy-4-phenylcoumarin, prepared either by the action of acetyl chloride and acetic acid on 2:4-dimethoxy-$\beta\beta$-diphenylacrylic acid or by condensing ethyl benzoylacetate with resorcinol monomethyl ether. Reduction of the coumarin with sodium and alcohol (Semmler, *Ber.*, 1906, **39**, 2856) gives 2:4-dimethoxy-$\beta\beta$-diphenylpropyl alcohol which on treatment with a saturated alcoholic solution of hydrochloric acid gives 7-methoxy-4-phenylchroman.

For the preparation of 7-methoxy-4-(3′:4′-dimethoxy)phenylchroman, the starting point is the corresponding coumarin which may be obtained either from 2:4:3′:4′-tetramethoxy-$\beta\beta$-diphenylacrylic acid or by condensing ethyl veratroylacetate with resorcinol monomethyl ether, the second method giving a better yield.



Reduction with sodium and alcohol gave a product, probably the propyl alcohol derivative, which could not be obtained in an analysable condition. On heating with an alcoholic solution of hydrochloric acid saturated at 0° for three to four hours at 100°, the chroman was obtained.

Experimental.

Ethyl β-Hydroxy-2:4-dimethoxy-ββ-diphenylpropionate.—2:4-Dimethoxybenzophenone (24 g.), ethyl bromoacetate (21 g.), zinc turnings (8·5 g.) and benzene dried over sodium (96 c.c.) were mixed in a flask fitted up with a reflux condenser and heated cautiously over the wire-gauze. Once started the reaction proceeds even without heating. It is complete in about three hours when the zinc goes almost entirely into solution and the originally light yellow mixture changes to a deep brown oily liquid. After cooling, the product is poured into ice-cold dilute sulphuric acid kept in a separating funnel and shaken vigorously. The benzene layer containing the condensation product is separated, dried with anhydrous sodium sulphate and the benzene distilled off. The residue solidifies on cooling; needles from alcohol, m.p. 79-80°. (Found: C, 68·77; H, 7·17. $C_{19}H_{22}O_5$ requires C, 69·09; H, 6·7 per cent.).

Ethyl 2:4-Dimethoxy-ββ-diphenylacrylate.—The dehydration of the oxy-ester could be effected neither by treatment with acetic anhydride and fused sodium acetate (Rupe and Busolt, *Ber.*, 1907, **40**, 4537) nor by acetic anhydride and acetyl chloride (Stoermer and Friderici, *Ber.*, 1908, **41**, 333) but complete dehydration took place on subjecting it to dry distillation under diminished pressure. It melts first to a light brown liquid and then blackens. Water drops begin to distil and finally the cinnamic acid derivative distils as a reddish-brown thick oily liquid. On redistilling, a straw-coloured thick oily liquid, b.p. 228-232°/11 mm. was obtained. (Found: C, 72·64; H, 6·4. $C_{19}H_{20}O_4$ requires C, 73·07; H, 6·41 per cent.).

2:4-Dimethoxy-ββ-diphenylacrylic Acid.—The acid was obtained by hydrolysing the ester (10 g.) with 25% methyl alcoholic potash (20 c.c.) on the water-bath under reflux for 24 hours. The reaction product was diluted with water and after removal of methyl alcohol by heating on the water-bath the unchanged ester was extracted with ether. The acid was precipitated by acidification with hydrochloric acid. Prisms from alcohol, m.p. 169-70°. (Found: C, 71·63; H, 6·01. $C_{17}H_{16}O_4$ requires C, 71·83; H, 5·63 per cent.).

7-Methoxy-4-phenylcoumarin.—2:4-Dimethoxy-ββ-diphenylacrylic acid (10 g.) was dissolved in glacial acetic acid (40 c.c.) in a stoppered bottle, freshly distilled acetyl chloride (10 c.c.) added and allowed to stand for 24 hours. The faint red colour of the mixture changed

gradually to deep violet. It was poured on crushed ice, the precipitate washed with sodium carbonate solution and recrystallised from alcohol as long needles, m.p. 114-15°. The same coumarin derivative was also obtained by methylation of the condensation product of ethyl benzoylacetate with resorcinol (Pechmann and Hanke, *Ber.*, 1901, **34**, 856). (Found: C, 75·91; H, 5·01. $C_{16}H_{12}O_3$ requires C, 76·19; H, 4·76 per cent.).

2:4-*Oxymethoxy-ββ-diphenyl propyl Alcohol.*—7-Methoxy-4-phenylcoumarin (5 g.) was dissolved in absolute alcohol (100 c.c.) previously distilled over metallic calcium, in a flask fitted with a condenser and a soda-lime guard-tube and metallic sodium (15 g.) added all at once. The reaction is very vigorous but subsides to some extent within five minutes, the vessel is then placed in an oil-bath, heated to 140-50° and the reaction is allowed to proceed till all the sodium had dissolved. For the success of the operation the system should be perfectly dry and the reaction mixture should in no case be allowed to solidify, further 50 to 75 c.c. of absolute alcohol being added if necessary. The reaction is complete in about three to four hours when, after cooling, 100 c.c. of water are added and the ethyl alcohol removed by passing steam. The residue is acidified with hydrochloric acid, extracted with ether, the ethereal extract washed with sodium bicarbonate solution, dried with anhydrous sodium sulphate and the ether distilled off. The residue is distilled under diminished pressure, b.p. 253°-254°/10 mm. It was found to solidify on standing for nearly a month ; m.p. 77-78°. (Found: C, 74·01; H, 7 01. $C_{16}H_{18}O_3$ requires C, 74·41 ; H, 6·97 per cent.).

7-*Methoxy-4-phenylchroman.*—The alcohol (3 g.) was dissolved in absolute alcohol (30 c.c.), saturated with dry hydrochloric acid gas and heated in a sealed tube at 100° for six hours. After cooling, the contents are poured into water, the alcohol removed by heating on the water-bath, cooled, and extracted with ether. The ethereal extract was washed with dilute caustic soda solution, dehydrated with anhydrous sodium sulphate and distilled under diminished pressure, b.p. 203°-204°/10 mm. (Found: C, 79·7; H, 7·17. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·66 per cent.).

2:4-*Dimethoxy-ββ-diphenylpropionic Acid.*—The corresponding acrylic acid was dissolved in the calculated quantity of 10% caustic soda solution and sodium amalgam (4·5 g. sodium in 180 g. of mercury) was gradually added in course of 3—4 hours with frequent shaking. The alkalinity was kept down by the addition of small

quantities of hydrochloric acid from time to time. After standing overnight the solution was decanted. On acidification an ash-coloured thick oil was precipitated which soon solidified. Rectangular plates from alcohol, m.p. 129-30°. (Found: C, 71·05; H, 6·48. $C_{17}H_{18}O_4$ requires C, 71·33; H, 6·29 per cent.).

Ethyl 2:4-*Dimethoxy-ββ-diphenylpropionate*.—The ester was prepared by saturating an absolute alcoholic solution of the acid with dry hydrochloric acid gas and heating under reflux on the water-bath for an hour. The ester was precipitated with water, dissolved in ether, filtered, washed with sodium carbonate solution. On evaporating the ether it remained as an oil which was re-dissolved in petroleum ether. On cooling in a freezing mixture it separated in flattened needles, m.p. 54°. (Found: C, 72·48; H, 7·19. $C_{19}H_{22}O_4$ requires C, 72·61; 7·06 per cent.).

2: 4:3′:4′-*Tetramethoxybensophenone*.—Aluminium chloride (10 g.) was added to a mixture of veratroyl chloride (10 g.) and resorcinol dimethyl ether (30 c.c.) with constant shaking, the temperature being kept below 40°. The excess of resorcinol dimethyl ether was removed by repeated extraction with carbon bisulphide and finally the condensation product was decomposed cautiously by warming with dilute hydrochloric acid on the water-bath for ten minutes. The ketone was treated for a few minutes with hot caustic soda solution and the residue recrystallised from alcohol; prisms, m.p. 126°. (Found: C, 67·19; H, 6·1. $C_{17}H_{18}O_5$ requires C, 67·54; H, 5·96 per cent.).

2: 4: 3′: 4′-*Tetramethoxy-ββ-diphenylacrylic Acid*.—2: 4: 3′: 4′-Tetramethoxybenzophenone (10 g.), ethyl bromoacetate (7 g.), zinc turnings (2·8 g.) and benzene dried over sodium (50 c.c.) were heated cautiously under reflux over the wire-gauze. The reaction is complete in about three hours when the product assumed a brown jelly-like appearance. It was cooled and decomposed by shaking with ice-cold dilute sulphuric acid in a separating funnel. The benzene layer was dried over anhydrous sodium sulphate and the benzene evaporated when a thick brown oily liquid was obtained. A portion of the condensation product (5 g.) was hydrolysed with 25% methyl alcoholic potash (10 c.c.) on the water-bath for twenty-four hours. Another portion was dry-distilled in *vacuo* and the distillate (5 g.) hydrolysed as before. The products were found to be identical, both melting at 157° after crystallisation from alcohol. (Found: C, 66·40; H, 6·28. $C_{19}H_{20}O_6$ requires C, 66·28; H, 5·81 per cent.).

2 : 4 : 3′ : 4′-*Tetramethoxy-ββ-diphenylpropionic Acid.*—The acrylic acid derivative (4·5 g.) was dissolved in the calculated quantity of 10% caustic soda solution and sodium amalgam made by dissolving sodium (1·2 g.) in mercury (45 g.) was gradually added with frequent shaking. The addition is complete in about two hours and the mixture is allowed to stand overnight at the ordinary temperature. The alkaline liquid is decanted off and acidified with hydrochloric acid when the dihydro-acid is precipitated as an oil which soon solidifies; plates from alcohol, m.p. 121°. (Found: C, 66·06; H, 6·6. $C_{19}H_{22}O_6$ requires C, 65·89; H, 6·35 per cent.).

7-*Methoxy*-4-(3′ : 4′-*dimethoxy*) *phenylcoumarin.*—2 : 4 : 3′ : 4′-Tetramethoxy-ββ-diphenylacrylic acid (5 g.) was dissolved in glacial acetic acid (20 c.c.), cooled to about 5° and freshly distilled acetyl chloride (5 c.c.) was added and allowed to stand at ordinary temperature for 24 hours. The product which had assumed a resinous appearance was poured into crushed ice and the precipitate filtered, washed and crystallised from alcohol, m.p. 163°. As the yield was very small, an alternative method of preparation was attempted. Ethyl veratroylacetoacetate was prepared by condensing veratroyl chloride with ethyl sodioacetoacetate in ethereal solution (*Beilstein*, *II, 958). The product was hydrolysed with 10% ammonium hydroxide solution at 40°-50° for 15 minutes. The veratroylacetic ester separated as an oil which was extracted with ether, washed with water and dried over anhydrous potassium carbonate. The ester could not be obtained in an analysable condition as it boils with decomposition above 200° at 10 mm. It is freed from its lower-boiling impurities by heating at 140° for half an hour at 10 mm. The purified ester (5 g.) was mixed with resorcinol monomethyl ether (2·6 g.), cooled well in ice and ice-cold pure sulphuric acid (15 c.c.) was added in about one and a half hours' time. The mixture was allowed to stand in an well-stoppered bottle and after 12 hours poured into crushed ice. The semi-solid mass was treated with dilute caustic soda solution and crystallised from alcohol as needles, m.p. 168° which is not depressed by admixture with the product obtained by the first method. (Found: C, 69·10 ; H, 5·43. $C_{18}H_{16}O_5$ requires C, 69·23; H, 5·12 per cent.).

7-*Hydroxy*-4(3′ : 4′-*dimethoxy*)*phenylcoumarin.*—Purified ethyl veratroyl acetate (2 g.) and resorcinol (1·1 g.) was treated with sulphuric acid as in the previous case and the product crystallised from alcohol ; needles, m.p. 286°. (Found: C, 68·72; H, 5·14. $C_{17}H_{14}O_5$ requires C, 68·45; H, 4·69 per cent.). Methylation with dimethyl

sulphate gives 7-methoxy-4(3′: 4′-dimethoxy)phenylcoumarin, m.p. 163°.

7-Methoxy-4(3′: 4′-dimethoxy)phenylchroman.—The coumarin (5 g.) was dissolved in 150 c.c. absolute alcohol and metallic sodium (15 g.) added in three instalments. The mixture is heated in an oil-bath at 140-50° for three hours when nearly the whole of the sodium practically dissolved. Rectified spirit (50 c.c.) was next added to dissolve any unreacted sodium. The mixture was dissolved in water and the alcohol removed by passing steam. It was then cooled, acidified with hydrochloric acid when a viscous oil was precipitated. The oil was taken up with ether and the extract treated twice with 2% caustic soda solution. On acidification with hydrochloric acid a gummy precipitate was obtained which solidified after 24 hours but which could not be crystallised from any solvent. The crude product was heated in a sealed tube at 100° with alcohol saturated with hydrochloric acid, for 3—4 hours. The reaction product was then poured into water, extracted with ether and the ethereal extract washed with 2% sodium hydroxide solution to remove unreacted and partially demethylated product, dried with calcium chloride and the ether evaporated. As the substance showed no tendency to solidify even after long standing it was distilled under diminished pressure when the chroman was obtained as an oil, b.p. 263°-266°/4 mm. (Found: C, 71·73; H, 7·23. $C_{18}H_{20}O_4$ requires C, 72·00; H, 6·67 per cent.).

The work will be continued.

UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA.

Received February 23, 1931.

Strainless Monocyclic Rings. Part I. Isomerism of 4-Methyl*cyclo*hexane-1-carboxy-1-acetic Acid. Some Evidences of Strainless *cyclo*Hexane Ring.

By Mahammad Qudrat-i-khuda.

From a consideration of the closed carbon rings on the model it is evident that in the case of three, four and five membered rings the carbon tetrahedra are incapable of free rotation round their valency bonds, these rings will thus be co-planar and consequently more or less strained ones, whereas in six and higher membered rings this rotation is possible ; and then the planar and highly strained structures for these rings may no longer exist, the strained form passing into the strainless multiplanar configuration. For a *cyclo*hexane ring this spatial structure free from strain has been found by Mohr (*J. pr. Chem.*, 1918, **98**, 315) and Sachse (*Ber.*, 1890, **23**, 1368) to be capable of existing in two modifications represented by a boat and a chair-shaped configuration.

According to the modern conceptions, the molecules of any substance are dynamic *i.e.*, they are moving incessantly. Mohr (*loc. cit.*) concluded from an examination of the models that the strain involved in the interconversion of Sachse's strainless forms of *cyclo*hexane ring is so slight that it is overcome by this inter-molecular collision which brings about the intra-molecular rotation in the carbon atoms of the rings and hence, although theoretically possible, the two forms of *cyclo*hexane itself have not yet been isolated, one being easily converted into the other. The passage of one into the other form, however, will necessitate an intermediate structure which is planar and consequently a strained one.

This will be the state of affairs unless at least two of the carbon atoms in the ring are substituted which may bring about a sort of check to the free rotatory motion of the atoms inside the molecule, resulting in the total arrest or a tendency towards arrest of the intra-molecular motion stabilising it in one or the other isomeric modifications of the same compound, which may then be capable of being isolated. The case of dacahydronaphthalene can be taken as a specific illustration of this hypothesis; here, the taking part of two carbon atoms of one six-membered ring in the formation of an

adjacent six-carbon structure causes a complete arrest of the intramolecular rotatory motion of all the carbon atoms round their valency bonds, rendering the molecule static so far as the internal motion is concerned. Justification of the hypothesis has been very adequately supplied by the observations of Hückel and his collaborators (Hückel, *Annalen*, 1925, **441**, 1; 1927, **415**, 109; Hückel and Friedrich, *ibid*, 1926, **451**, 132; Hückel and Stepf, *ibid*, 1927, **463**, 168), who very successfully isolated the various isomeric derivatives of decahydronaphthalene as necessitated by the theory. While discussing the *cyclo*hexane ring in particular, it should be mentioned here that either in *cyclo*hexane molecule itself or in any monosubstituted *cyclo*hexane compound, the factor which arrests the free rotational motion of the carban tetrahedra is either absent or is only very feeble. Also it should be mentioned that the energy required to overcome the resistance in the interconversion of the two strainless forms in *cyclo*hexane is only very slight; the consequence is that up till now no evidence of the strainless *cyclo*hexane ring has been obtained. Several workers have investigated into the matter but apparently without success. Unfortunately in their investigations they did not take notice of this particular factor which alone can stabilise the different stereoisomeric forms (compare *e.g.* Wightmann, *J. Chem. Soc.*, 1926, p. 2541). Chavanne and Becker (*Bull. Soc. Chim. Belg.*, 1922, **31**, 95) carried out some experiments on the reduction of the three xylenes and particularly in the case of the *ortho* compound they observed that different products were obtained by using nickel and platinum as catalysts in the hydrogenation processes. The isomerism may be of the ordinary kind, which is explicable on the assumption of a planar structure for the *cyclo*hexane ring and which is caused by the different positions of methyl groups and hydrogen atoms with respect to the plane of the ring, just as has been observed to be the case with hexahydro-*p*-toluic acid (I) (Einhorn and Willstätter, *Annalen*, 1894, **280**, 160) or it might be due to the existence of multiplanar configuration of the *cyclo*hexane ring, when not only these but two more stereoisomers will be capable of existence. It has not been definitely settled, however, whether the isomerism of these hydrogenated xylenes is of the former or latter type. The separation and characterisation of these dimethyl*cyclo*hexanes does apparently involve a good deal of difficulty. In order to establish definitely the truth of the hypothesis in question, attention has now been directed towards the synthesis and separation of

some other derivatives of *cyclo*hexane, in which at least two of the carbon atoms are more or less heavily substituted, so that the molecular volume of the substituents exert influences which may be effective enough in stabilising the strainless configurations and render it possible to isolate the different isomeric derivatives as necessitated by the hypothesis.

If, by virtue of the heavy substituents, the *cyclo*hexane molecule is rendered static in the puckered forms, then only, on consideration of models, it will be found that a compound of the type (II) should exist in four stereoisomeric modifications (Figs. I, II, III and IV respectively), two of them will have the boat (Figs. I and II) and the other two the chair-shaped (Figs. III and IV) configurations. If we were to term the former pair *cis* and the latter *trans*-structures then again the *cis* compound will have either a *cis-cis* or *cis-trans* configuration according as the substituents R and X lie on the same or opposite directions of the plane occupied by the four carbon atoms marked with asterisk and lying in a plane perpendicular to it. Similarly the second set of compounds would be called *trans-cis* and *trans-trans* isomers with respect to the position occupied by the substituents R, X, R/ and Y.

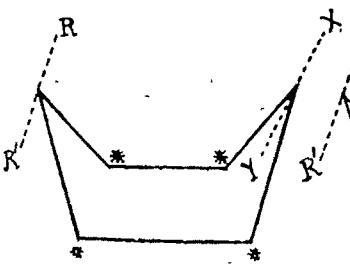


Fig. I.

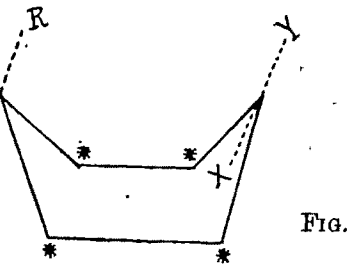


Fig. II.

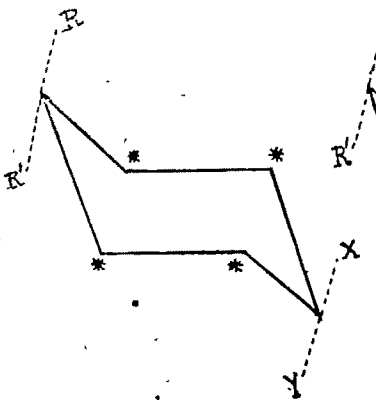


Fig. III.

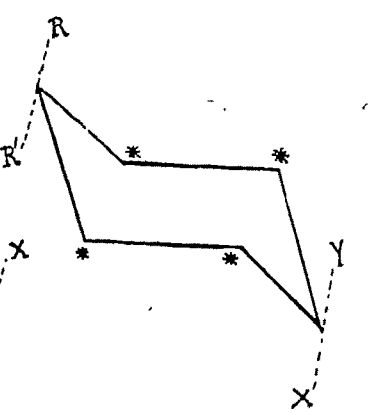
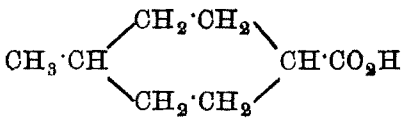
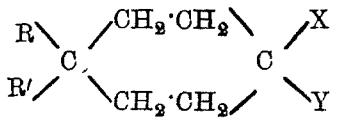


Fig. IV.



(I)

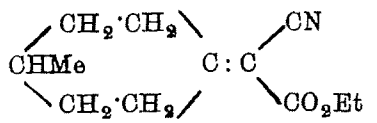


(II)

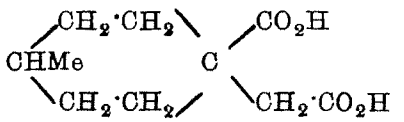
In these compounds by virtue of the molecular volumes of the substituents R, R′, X and Y, as discussed above, there will be a tendency to prevent the internal motion of the molecule and make it possible to isolate all the four stereoisomers which might or might not be convertible into one another, according as the molecular volumes of the substituents are bulky enough to arrest the intramolecular motion completely or not.

An acid (V) corresponding to the type (II) has now been prepared and it has been possible to isolate all the four probable isomers of the same. As at present we have no means to classify them and definitely assign a *cis-cis* or a *cis-trans* structure to one or the other of these compounds they have provisionally been named as acids A, B, C and D respectively.

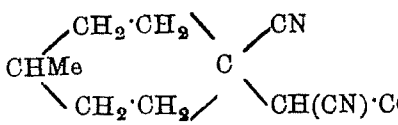
4-Methyl*cyclo*hexanone condenses well in presence of piperidine with ethyl cyanoacetate, yielding the unsaturated cyano-ester (III). This ester, when condensed with potassium cyanide according to the method of Lapworth and McRae (*J. Chem. Soc.*, 1922, **121**, 2741) in alcoholic solution, yields the dicyano-ester (IV), which on hydrolysis with concentrated hydrochloric acid gives a mixture of the isomeric acids of the constitution (V), a compound which is similar to that represented by the formula (II), where R=Me, R′=H, X=CH_2.CO_2H and Y=CO_2H.



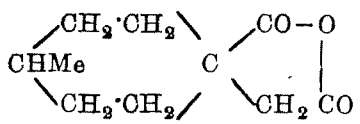
(III)



(V)



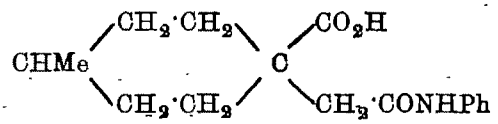
(IV)



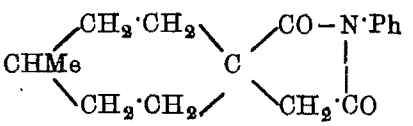
(VI)

The process of separation of these acids is a tedious and difficult one, but when the details enumerated in the experimental portion are strictly adhered to, they can be obtained in four distinct modifica-

tions. All these acids yield anhydrides (VI), which should also exist in four stereoisomeric forms, for which multiplanar structures according to the configurations of the acids can be assigned. In fact, all these anhydrides have been isolated of which three are solids melting respectively at 77°, 59° and 104° while the fourth is a liquid under ordinary conditions. From each of these acids different anilic acids (VII) have been obtained melting at 195°, 185°, 183° and 184° respectively and from three of these different anils (VIII) have also been prepared. The acids themselves, however, melt respectively at 137°, 129°, 174° and 146°.

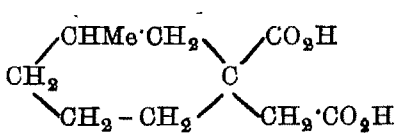


(VII)

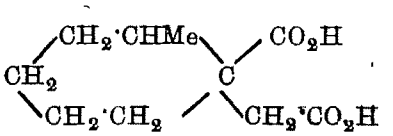


(VIII)

There was just a possibility that some of these acids might have been derived from the other isomeric methyl*cyclo*hexanones which might have been present along with the *para*-ketone used, as impurity. To eliminate this possibility, the acids (IX) and (X) have also been synthesised from the corresponding ketones, and the acids so far obtained do not appear to be similar to any of these four acids. A description of these, however, is reserved for a future communication.



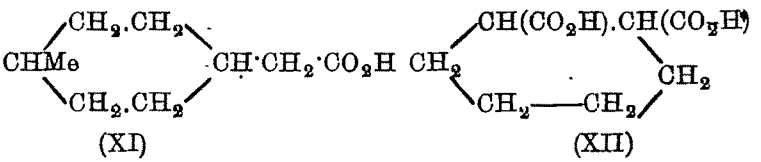
(IX)



(X)

It is doubtful whether the conditions for stabilishing the strainless forms in the acid (I) and other similar acids such as *p*-methyl*cyclo*hexaneacetic acid (XI) (Wallach and Evans, *Annalen*, 1907, **353**, 313; Perkin and Pope, *J. Chem. Soc.*, 1908, **93**, 1075) are fully present in them. Like hexahydrophthalic acid (XII) (Baeyer, *Annalen*, 1890, **258**, 218) these acids have so far been found to occur in not

more than two stereoisomeric forms; a detailed andmore searching examination has already been undertaken with these acids along with a series of similar compounds of different types and the results will be communicated in due course.



(XI) (XII)

EXPERIMENTAL.

Ethyl *p*-methyl*cyclo*hexylidenecyanoacetate was prepared with slight modification of the method of Hardinge, Haworth and Perkin (*J. Chem. Soc.*, 1908, 93, 1958) thus: *p*-Methyl*cyclo*hexanone (224 g.) and ethyl cyanoacetate (226 g.) were mixed together and to the mixture 4 c.c. of piperidine were added, when the mixture became warm and globules of water began to separate. This was left for 40 hours at the ordinary temperature and then heated on the steam-bath for two hours. To the mixture was then added excess of water and the solution acidified with hydrochloric acid and the oil that was precipitated was taken up in ether, washed and dried over calcium chloride and then fractionated in a vacuum. At first some unchanged ketone and cyano-ester come over and then the unsaturated ester distils at 166°/13 mm. The unchanged mixture of ketone and cyano-ester was treated again with 3 c.c. of piperidine and worked up as described above, when some more of the same unsaturated cyano-ester was obtained (total yield 80%). When re-distilled the ester had b. p. 165°/12 mm.; $d_4^{16\cdot4^\circ} = 1\cdot02877$, $n_D^{16\cdot4^\circ} = 1\cdot49118$ whence $[R_L]_D = 58\cdot29$ (calc. 56·36). The exaltation is due to the presence of a conjugated system.

Ethyl 4-Methylcyclohexane-1-cyano-1-α-cyanoacetate.—The addition of potassium cyanide to the unsaturated cyano-ester (III) was effected according to the method of Lapworth and McRae (*loc. cit.*) with some modifications, mainly on the line of those adopted by Bardhan (*J. Chem. Soc.*, 1928, p. 2591) which briefly is as follows. The unsaturated ester (100 g.) was dissolved in rectified spirit (480 c.c.) and to this was added a solution of potassium cyanide (54 g.) in water (135 c.c.). The solution became hot soon after the addition of potassium cyanide and after 24 hours scaly shining crystal of

the potassium salt of the addition compound began to separate. This was left to stand for 8 days in order to allow the reaction to be complete. The alcohol was then removed on the water-bath and finally under reduced pressure. The coloured residue of the salt of the dicyano-ester was then hydrolysed without being isolated.

Hydrolysis of the Dicyano-ester (IV): *Preparation of the Mixture of the Succinic Acids.*—The dark coloured residue obtained in the previous experiment was hydrolysed with 700 c.c. of concentrated hydrochloric acid by heating for 8-9 hours with a reflux condenser. The solution was then cooled, diluted and extracted with ether. The acid was removed from the ethereal extract by washing with a solution of sodium carbonate. The ethereal solution gave some solid neutral product which could be crystallised from hot water or dilute alcohol when it melted indefinitely at 139-44° and appeared to be mixture of the imides of the succinic acids.

The alkaline solution on being acidified with dry hydrochloric acid precipitated an acid which was taken up in ether, dried and the solvent removed, when it was obtained as a solid of indefinite melting point. The yield of the acid is 50 g.

Separation of the Acids.—The crude mixture of acids was neutralised with a solution of ammonia and the clear solution was evaporated on the water-bath to dryness. The dry ammonium salt was then extracted with enough hot absolute alcohol and filtered off. The solid on the filter funnel was washed several times with small quantities of the hot solvent. The solid thus obtained was dried in the air and then treated with water, when excepting a negligibly small residue the whole of it dissolved. The clear filtered solution was acidified and extracted with ether. The dried ethereal extract left a solid which did not appear to be quite pure neither could purification of it be effected by fractional crystallisation. The whole of the acid was, therefore, refluxed for two hours with a slight excess of acetic anhydride and the product was fractionated in a vacuum. On removing the acetic acid and the excess of acetic anhydride, the anhydride of the succinic acid was obtained which distilled at 154°/12 mm. and set to a hard crystalline mass in the receiver. The crude anhydride melted indefinitely at 55-60°. This was then crystallised from petroleum (b.p. 60-80°) when two kinds of crystals were obtained. Those that separated at first are hard and heavy rhombic cubes. At a certain stage the crystallisation of this fraction is almost complete. If care is taken to watch the

solution at this stage, the supernatent liquid can be decanted off at this point and these crystals can then be purified by one more crystallisation from the same solvent. Or else, if only one crystal of the second anhydride separates out, the whole of it is thrown out of solution in rapid succession. This second anhydride is in appearance purely white flakes and is very light. It is, therefore, possible to separate them mechanically by shaking with cold petroleum and decanting the solution, when the first formed heavy crystals sink to the bottom and usually do not come along with these. By careful manipulation, however the two can thus be obtained as distinct solid bodies, which are quite pure after two or three crystallisations.

The Acid A.—The first of these anhydrides, say the anhdride of the acid (A), melts at 77°. (Found: C, 66·0 ; H, 7·9. $C_{10}H_{14}O_3$ requires C, 65·9 ; H, 7·7 per cent.).

The acid (A) itself was obtained from this anhydride by hydro'ysing it with diltue caustic soda solution. It crystallises well from benzene and melts at 137°. (Found: C, 60·0 ; H, 8·0; M. W. by titration, 200. $C_{10}H_{16}O_4$ requires C, 60·0 ; H, 8·0 per cent. M. W., 200).

The *anilic acid* was obtained by adding a solution of aniline (1 mol.) in benzene to a benzene solution of the anhydride, m. p. 77° (1 mol.). After a few minutes some crystalline solid separated which dissolved completely in a solution of dilute sodium carbonate. The alkaline solution on acidification gave the free anilic acid, which crystallises from dilute alcohol in long prismatic needles and melts at 195°. (Found: C, 70·0 ; H, 7·8. $C_{16}H_{21}O_3N$ requires C, 69·8 ; H, 7·6 per cent.).

The *anil* was prepared by heating this anilic acid at 200-10° for about 15 minutes. The melt was cooled, washed with a solution of sodium carbonate and water and then crystallised from alcohol when it separated in short needles, m. p. 130°. (Found: C, 74·4 ; H, 7·4. $C_{16}H_{19}O_2N$ requires C, 74·7 ; H, 7·4 per cent.).

The *imide* was obtained by heating the dry ammonium salt of the acid (A), in a test tube for some time on a very small flame. When the decomposition was complete, which took about 20 minutes to half an hour, the melt was cooled and the solid thus obtained was washed with water, dilute sodium carbonate solution and again water and was crystallised from dilute alcohol, when it

came out in thin lustrous laminae, m. p. 119-20°. (Found: C, 66·6; H, 8·2. $C_{10}H_{15}O_3N$ requires C, 66·3; H, 8·3 per cent.).

p-*Toluidinamic acid* was precipitated when solutions of the anhydride and *p*-toluidine in benzene were mixed together in molecular proportion. The solid which is completely soluble in a solution of sodium carbonate, was purified by crystallisation from dilute alcohol, when it melted at 199°. (Found: C, 71·0; H, 7·8. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 7·9 per cent.).

p-*Toluidinimide* was prepared by heating the above *p*-toluidinamic acid at about 210-15°. When the decomposition was complete, the melt was cooled, washed with a solution of dilute sodium carbonate and water and then crystallised from alcohol, when it melts at 119°. (Found: C, 75·7; H, 7·8. $C_{17}H_{21}O_2N$ requires C, 75·3; H, 7·8 per cent.).

β-Naphthylamic Acid was obtained from the corresponding anhydride in a way similar to the other amic acids. It crystallises from dilute alcohol and melts at 200°. (Found: C, 74·2; H, 6·9. $C_{20}H_{23}O_3N$ requires C, 73·8; H, 7·0 per cent.).

β-Naphthylimide was obtained from the corresponding napthylamic acid in the usual way. It crystallises from dilute alcohol and melts at 162°. (Found: C, 78·8; H, 6·7. $C_{20}H_{21}O_2N$ requires C, 78·4; H, 6·8 per cent.).

The Acid (*B*).—As mentioned above the second anhydride, *i.e.*, the anhydride of the acid (B), was obtained from the petroleum mother-liquor of the anhydride of the acid (A), m. p. 77°. This was re-crystallised from the same solvent when it was obtained in thin lustrous laminae and melted at 59°. (Found: C, 65·7; H, 7·7 per cent.).

The *acid* (B) itself was obtained from the anhydride (m. p. 59°) by alkaline hydrolysis and was crystallised from benzene, from which it separated in prismatic needles, m. p. 129°. (Found: C, 60·0; H, 7·8 per cent. M. W. by titration, 200.).

The corresponding *anilic acid* was prepared in a way similar to that in the previous case. It crystallises from the same solvent and melts at 183°. (Found: C, 70·0; H, 7·5 per cent.)

The *anil* obtained by the usual method crystallised from alcohol and melted at 142-43°. (Found: C, 74·6; H, 7·5 per cent.).

The *imide* was isolated as the product of decomposition of the dry ammonium salt of the pure acid obtained from the anhydride, m. p. 59°. It crystallises in beautiful needles from hot water or

better from very dilute alcohol and melts at 130°. (Found: C, 66·7 ; H, 8·1 per cent.).

p-*Toluidinamic acid* resulted from the anhydride, m. p. 59°, and *p*-toluidine in the usual way. It crystallises from dilute alcohol and melts at 174°. (Found: C, 71·1 ; H, 7·9 per cent.).

p-*Toluidinimide* was obtained by the decomposition of the above *p*-toluidinamic acid a few degree above its melting point and crystallised from alcohol m. p. 134°. (Found: C, 75·7 ; H, 7·9 per cent.).

β-Naphthylamic acid prepared in the usual method crystallises from dilute alcohol and melts with decomposition at 192°. (Found: C, 74·2 ; H, 6·8 per cent.).

The corresponding *β-naphthylimide* crystallises from alcohol and melts at 144°. (Found: C, 78·7 ; H, 6·7 per cent.).

The Acids (C) and (D).—The alcoholic mother-liquor from the mixed ammonium salts was cooled when some crystalline solid was obtained. This was treated with water, which dissolved it partially and the insoluble substance appeared to be a neutral product containing nitrogen, this is probably an imide but is found to be different from those described above. On hydrolysis this imide gave an acid melting at 174° which is identical with the acid of the same melting point described below.

The cold alcoholic mother-liquor was now heated on the water-bath to remove the solvent and the small quantity of residue was preserved and after several experiments worked up as follows. The slightly pasty mass was treated with water and the traces of insoluble oily impurity removed by ether and the aqueous solution acidified and extracted with the same solvent. This latter ethereal solution left a semi-solid mass on removal of the solvent, which was extracted with hot benzene when some crystalline solid was left behind and the rest went into solution. The benzene solution was cooled with constant shaking and then filtered off. The solid which is practically insoluble in cold benzene was found to be an acid (*acid C*) isomeric with the two described above. It crystallises from acetic acid in stout prisms and melts at 174°. (Found: C, 60·0; H, 8·0 per cent. M. W. by titration, 200).

The *anhydride* of this acid was obtained by heating the acid (8 g.) with acetyl chloride (10 c.c.) on the water-bath for some time. Hydrogen chloride was given off and the acid went into solution. The excess of acetyl chloride and acetic acid was removed by evaporation on the water-bath and the residue was left

in an evacuated desiccator over caustic potash for a few days, when a solid anhydride was obtained. It crystallises in large shimmering plates from petroleum (b. p. 75-95°) and melts at 104°. (Found: C, 65·8 ; H, 7 6 per cent.).

The *anilic acid* prepared from this anhydride crystallises from alcohol and melts at 185°. (Found: C, 70·5 ; H, 7·8 per cent.).

The corresponding *anil* obtained in the usual way melts at the same temperature as the anilic acid itself namely 185° but it is insoluble in a solution of sodium carbonate while the other dissolves in it completely. (Found: C, 75·0 ; H, 7·2 per cent.).

The Acid (D).—From the benzene mother-liquor of the acid (C) the solvent was evaporated off on the water-bath and the residual gummy product was treated with petroleum (b. p. 75-95°) while the mass was still hot, when some crystalline solid separated out. This was treated with cold benzene which dissolved it practically completely leaving only traces of the acid (C). On the addition of petroleum to this cold benzene solution the fourth acid crystallises out after some time. This was re-crystallised from the same solvent and finally crystallised from hot water when it melted at 146°. (Found: C, 60·3 ; H, 7·8 per cent. M. W. by titration, 200).

The acid on being treated with acetyl chloride gave a liquid *anhydride*, which on being mixed with aniline gave an *anilic acid* melting at 184°. (Found: C, 70·5 ; H, 8·0 per cent.).

The petroleum mother-liquor from the fourth acid on removal of the solvent left a small amount of a viscous mass which has not yet been examined.

I desire to mention here that part of this work was done in the laboratory of Prof. J. F. Thrope, C.B.E., F.R.S., D.Sc., at the Imperial College of Science and Technology, South Kensington, London.

Organic Chemistry Laboratory,
Presidency College, Calcutta.

Received February 18, 1931.

A Note on the Vanadates of Heavy Metals.

By M. B. Rane and K. Kondiah.

Of the earlier investigations on the vanadates of metals, the pioneer work of Roscoe (*Phil. Trans.*, 1870, **160**, 317), Manasse (*Chem. Zentr.*, 1886, 773) and of Ditte (*Compt. rend.*, 1887, **104**, 1705) may be mentioned. Recently Ephraim and Beck (*Helv. Chim. Acta*, 1926, **9**, 38) prepared the vanadates of Ni, Co, Cu, Be, Zn, Mn, etc., by the double decomposition of the corresponding metallic sulphates by barium acid vanadate, which thus gave rise to complex salts, having the general formula $2MO, 3V_2O_5$, 12 or $15H_2O$ and less frequently $3MO, 5V_2O_5, nH_2O$. In the present investigation, the isolation, preparation and composition of vanadates of Hg, Au, Th, Ce and Zr are described.

Experimental.

The starting materials used in the preparation of the vanadate are ammonium *meta*-vanadate, obtained by careful crystallisation from an ammoniacal solution of V_2O_5 and potassium *pyro*-vanadate, obtained by fusion of two molecules of K_2CO_3 with one molecule of V_2O_5 in a platinum crucible, which was subsequently lixiviated with water and crystallised and washed free from carbonate. All the chemicals used were Merck's extra pure materials.

Carnot (*Compt. rend.*, 1887, **105**, 119) obtained an orange coloured substance by the action of mercurous nitrate on a soluble vanadate. Treadwell (Qualitative Analysis, 1927, p. 545) however, describes mercurous vanadate as white in neutral solution. In the present investigation, the same orange-coloured compound was obtained by the action of mercurous nitrate with ammonium vanadate. On analysis, the composition of the compound has been found to be the same as given by Carnot (*loc. cit.*). With a large excess of ammonium vanadate however, the colour of the compound is almost dark brown to black containing excess of V_2O_5. This is probably due to the presence of metallic mercury in a very fine

state, resulting from the partial decomposition of the mercurous vanadate.

Mercuric Vanadate.—Carnot (*loc. cit.*) failed to obtain any precipitate with $HgCl_2$ and alkali vanadate in the acid solution, but obtained a white and pale yellow precipitate in neutral and alkaline solutions respectively. In the present investigation, although no precipitate was obtained even on boiling the mixture of ammonium vanadate and mercuric chloride, a golden yellow precipitate was readily thrown down on addition of alcohol. The precipitate was, however, found to pass into the colloidal state on washing with water. The same precipitate was easily obtained by using alcoholic solution of mercuric chloride. The precipitate, though amorphous at first, soon becomes granular and when observed under a microscope appears crystalline, having a yellow colour in the transmitted light and a greenish tinge in reflected light. The preparation of this compound, however offers no difficulty if the nitrate of mercury is used instead of the chloride. The mercuric vanadate is found to be soluble in mineral acids, but not in acetic acid. It is also soluble in alkali chloride but not so in the nitrate. This explains the reason why Carnot failed to obtain the precipitate of the vanadate with mercuric chloride, and why it is so readily obtained with the nitrate. The alkali chloride peptises the precipitate, which thereby passes into the colloidal state. On heating, mercuric vanadate darkens in colour and finally decomposes at about 250°, mercury volatilising and V_2O_5 remaining behind. In order to determine the composition of the dried compound, mercury was determined as sulphide and vanadium estimated volumetrically in the filtrate. (Found: V_2O_5, 29·74 ; HgO, 70·84. $2HgO, V_2O_5$ requires V_2O_5, 29·77 ; HgO, 70·23 per cent.). Thus mercuric vanadate has the composition $2HgO, V_2O_5$.

Mercury ortho-Vanadate.—A thick orange precipitate is obtained by the addition of excess of cold solution of potassium *ortho*-vanadate to mercuric nitrate. This compound is also soluble in alkali chlorides and mineral acids. On heating, this compound behaves like the *meta* compound. On analysis of the dried sample, its composition is found to approximate to the formula $3HgO, V_2O_5$. (Found: V_2O_5, 22·95 ; HgO (by difference), 77·05. $3HgO, V_2O_5$ requires V_2O_5, 21·9 ; HgO, 78·1 per cent.).

Gold Vanadate.—Hundeshagen (*Chem. Zeit.*, 1905, 29, 799) failed to obtain any precipitate by the action of vanadic acid or

vanadic compounds with solutions of gold. The present authors find that although no precipitate is obtained by the action of solutions of ammonium vanadate and gold chloride even on heating, the colour of the resulting solution deepens. A golden yellow precipitate is however thrown down in presence of alcohol or electrolytes like ammonium chloride, indicating thereby the colloidal nature of the compound formed before precipitation. The yellow compound is unstable and the colour changes on standing to black. On washing, the freshly prepared precipitate passes into the colloidal state carrying a negative charge as shown by cataphoresis. On heating in a closed tube, the dry precipitate darkens in colour, gives out ammonia and finally decomposes into gold and V_2O_5. A dried sample of the neutral freshly prepared compound gave on analysis the following results. (Found: Au_2O_3, 51·62 ; V_2O_5, 42·19 ; $(NH_4)_2O$ (by difference), 6·19. Au_2O_3, $(NH_4)_2O$, $2V_2O_5$ requires Au_2O_3, 51·55 ; V_2O_5, 42·39 ; $(NH_4)_2O$, 6·06 per cent.).

With potassium *ortho*-vanadate and gold chloride, however, a hydrated compound having the composition Au_2O_3, $2V_2O_5$, H_2O is obtained. (Found: Au_2O_3, 53·21 ; V_2O_5, 44·22 ; H_2O (by difference) 2·57. Au_2O_3, $2V_2O_5$, H_2O requires Au_2O_3, 53·67; V_2O_5, 44·16 ; H_2O, 2·27 per cent.).

Thorium Vanadate,—By the action of a solution of ammonium-*meta*-vanadate on a dilute solution of thorium chloride, Volck (*Z. anorg. Chem.*, 1894, **6**, 161) obtained a greenish yellow precipitate, which according to him on drying had the composition ThO_2, V_2O_5, $6H_2O$. The present authors obtained with thorium nitrate and ammonium *meta*-vanadate, a yellow compound that fades in colour on standing and on heating turns into a green mass, insoluble in dilute mineral acids. By treating with strong acids, V_2O_5 passes gradually into green solution and ThO_2 remains behind. With thorium chloride however, a heavy bright coloured substance is obtained, which does not lose colour on standing. The dried sample on analysis is found to approximate to the composition ThO_2, V_2O_5, H_2O. (Found: V_2O_5, 40·33 ; ThO_2, 56·74 ; H_2O (by difference), 2·93. ThO_2, V_2O_5, H_2O requires V_2O_5, 39·21 ; ThO_2, 56·92 ; H_2O, 3·87 per cent.).

Cerium Vanadate.—With ceric nitrate and excess of ammonium vanadate, a yellowish white precipitate is obtained. This rapidly changes to dark brown. With excess of ceric nitrate, no darkening

takes place. On using a satuarated solution of ceric sulphate, however, a beautiful light yellow precipitate is thrown down, which settles readily. The compound is crystalline and on heating in a closed tube, it loses water and decomposes leaving behind a mixture of CeO_2 and V_2O_5. The analysis of a dried sample shows the composition to be $3CeO_2$, V_2O_5, $9H_2O$. (Found : CeO_2, 59·90 ; V_2O_5, 21·15 ; H_2O (by difference), 18·95. $3CeO_2$, V_2O_5, $9H_2O$ requires CeO_2, 60·17 ; V_2O_5, 21·08 ; H_2O, 18·75 per cent.).

Zirconium Vanadate.—A thick gelatinous yellow precipitate is obtained on treating a solution of zirconium nitrate with excess of ammonium vanadate. This is soluble in mineral acids and the dried sample on ignition in a closed tube loses water and finally decomposes into ZrO_2 and V_2O_5.

CHEMICAL LABORATORIES,
BENARES HINDU UNIVERSITY,
BENARES.

Received February 23, 1931.

Coumaryl 6-*iso*Cyanate and its Reactions.

By Biman Bihari Dey and Tiruvenkata Rajendra Seshadri.

The action of an excess of carbonyl chloride on 6-aminocoumarin in cold dry benzene solution results in the formation of a mixture of coumaryl6 *iso*cyanate and aminocoumarin hydrochloride, the reaction being supposed to take place through the intermediate carbamyl chloride, thus:

(*i*) $2C_9H_5O_2\cdot NH_2 + COCl_2 = C_9H_5O_2\cdot NH\cdot COCl + C_9H_5O_2\cdot NH_2,HCl$

(*ii*) $C_9H_5O_2\cdot NH\cdot COCl = C_9H_5O_2\cdot N:C:O + HCl$ (*cf.* Werner, *J. Chem. Soc.*, 1918, **113**, 694).

If, however, the aminocoumarin employed be in excess, the reaction proceeds further and an almost theoretical yield of pure symmetrical dicoumarylcarbamide is obtained.

Coumaryl 6-*iso*cyanate is a crystalline solid dissolving readily in benzene and other solvents, and although it resembles phenyl *iso*-cyanate in most of its reactions, it is found to be relatively stabler and less reactive than the latter. When kept in contact with water it changes only slowly into dicoumarylcarbamide. The condensation with alcohols, phenols and amines is best carried out by warming on the water-bath, the resulting ethyl coumarylcarbamate and coumaryl-carbamides being usually mixed with a small amount of symmetrical dicoumarylcarbamide which is formed as a by-product. The latter is practically insoluble in boiling alcohol and is therefore easily separated from the main products of the reaction. Symmetrical dicoumarylcarbamide has also been obtained in an excellent yield by heating aminocoumarin and carbamide in glacial acetic acid solution (*cf.* Sonn, *Ber.*, 1914, **47**, 2440).

It is interesting to note that monocoumarylcarbamide and phenyl-coumarylcarbamide, which were prepared by reacting aminocou-marin with potassium cyanate and phenyl *iso*cyanate respectively, were found to be identical with those derived form the condensation

of coumaryl *iso*cyanate with ammonia and aniline respectively. It would appear, therefore, that Werner's unsymmetrical formulæ are inadmissible in these cases, the molecules in the static condition being symmetrical.

Both monocoumarylcarbamide and sym.-phenylcoumarylcarbamide decompose vigorously at their melting points: the former yields pure dicoumarylcarbamide as the only product of decomposition, while the latter gives rise to a mixture of symmetrical diphenylcarbamide and symmetrical dicoumarylcarbamide. The change is evidently to be explained by assuming that the decomposition proceeds in two different directions simultaneously, as follows:—

$$C_9H_5O_2\cdot NH\cdot CO\cdot NH_2 \longrightarrow \begin{cases} C_9H_5O_2\cdot NCO \\ \downarrow \\ C_9H_5O_2\cdot NH_2 \end{cases} \text{Condense.} \quad \begin{cases} + \text{ Escape. } NH_3 \uparrow & \ldots(1) \\ + \text{ Escape. } HNCO \uparrow & \ldots 2) \end{cases}$$

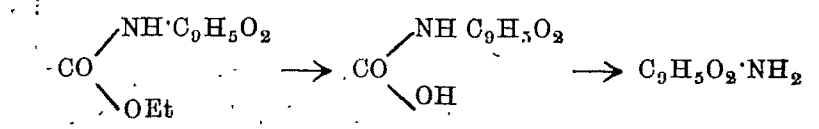
$$C_9H_5O_2\cdot NH\cdot CO\cdot NH\cdot C_6H_5 \longrightarrow \begin{cases} C_9H_3O_2\cdot NCO \\ \downarrow \\ C_9H_3O_2\cdot NH_2 \end{cases} \text{Condense.} \quad \begin{cases} + C_6H_5\cdot NH_2 \\ \downarrow \\ + C_6H_5\cdot NCO \end{cases} \text{Condense.} \quad \begin{matrix} (1) \\ (2) \end{matrix}$$

The products of decomposition then undergo new combinations among themselves so as to produce the stablest disubstituted carbamides. In the case of monocoumarylcarbamide, the purity of the dicoumarylcarbamide formed by its decomposition is presumably due to the readiness with which the other products, *viz.*, ammonia and cyanic acid, escape, leaving the residual aminocoumarin and coumaryl *iso*cyanate to react with each other.

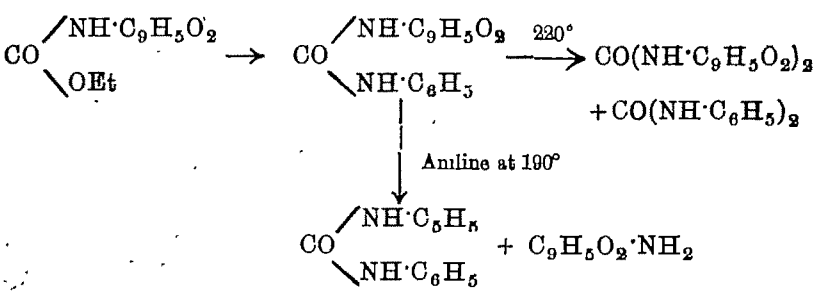
Ethyl coumarylcarbamate is remarkably stable and remains unattacked even on boiling with concentrated hydrochloric acid. Heating with acids under pressure brings about simple hydrolysis, 6-aminocoumarin being the sole product of the reaction. Ordinary ethyl carbamate (urethane) has been shown to be split up into *iso*cyanic acid and ethyl alcohol, the former being hydrolysed to ammonia which then combines with excess of *iso*cyanic acid to form carbamide, and these reactions have been adduced as evidence in favour of the imino-formula for urethane (Werner, *J. Chem. Soc.*, 1918, **113**, 622) which is assumed to decompose in the following manner:—

$$\cdot NH{=}C\begin{matrix} \diagup OEt \\ \diagdown OH \end{matrix} = HNCO + EtOH$$

In the present case, however, the hydrolysis obviously proceeds normally, not a trace of the insoluble dicoumarylcarbamide being isolated, thus:



The reaction of ethyl coumaryl-6-carbamate with aniline is interesting. No reaction is observed below 150°, but when the temperature is raised to 200°, and a molecular equivalent of aniline is employed, a mixture of diphenyl- and dicoumaryl-carbamides is formed. If, however, an excess of aniline (4 mols.) be used and the temperature maintained at 180-190° a mixture of diphenylcarbamide and 6-aminocoumarin is found to be produced to the complete exclusion of dicoumarylcarbamide. These observations may be explained by assuming the formation, in the first instance, of phenylcoumarylcarbamide which decomposed in the vicinity of its melting point (220°) in the manner indicated before. In the presence of a large excess of aniline and at a lower temperature, the influence of mass becomes prominent and the aniline simply displaces the aminocoumarin from its combination. The changes may be represented by the following equations:



4: 7-Dimethylcoumaryl 6-*iso*cyanate, which has been prepared in a similar manner, and some of its derivatives are also described here.

Experimental.

Coumaryl 6-iso*Cyanate*, $C_9H_5O_2{\cdot}NCO$.—6-Aminocoumrin (2 g.) suspended in a fine state in dry benzene (30 c.c.), was added slowly

with stirring to a solution of carbonyl chloride in toluene (20 per cent.) which was cooled in ice. A white cloudy precipitate was formed. After standing overnight at the laboratory temperature, the mixture was filtered, the residue extracted with cold benzene, and the combined filtrate concentrated. Colourless glistening prismatic needles of the *iso*cyanate were deposited, melting at 163°; the pure product weighed 0·5 g. (Found: C, 63·9; H, 2·9; N, 7·5. $C_{10}H_5O_3N$ requires C, 64·2; H, 2·7; N, 7·5 per cent.).

The residue insoluble in benzene dissolved almost completely on treatment with hot water leaving a small portion which was found to be dicoumarylcarbamide (m.p. 326°, decomp.). The filtrate, on rendering alkaline, yielded yellow crystals of 6-aminocoumarin weighing 1·2 g.

Coumaryl 6-*iso*cyanate can be preserved unchanged in well-oppered bottles. It is stable in dry air, but in moist atmosphere it slowly changes into dicoumarylcarbamide. Warm water rapidly hydrolyses it producing dicoumarylcarbamide and carbon dioxide.

Ethyl Coumaryl-6-carbamate (*6-Coumarylurethane*), $C_9H_5O_2 \cdot NH \cdot CO_2Et$.—This was prepared in two different ways: (*a*) Coumaryl *iso*cyanate was boiled with excess of absolute alcohol and the solution filtered and concentrated. The urethane separated in colourless rectangular plates melting at 156°. The small residue insoluble in alcohol was identified with dicoumarylcarbamide. (*b*) 6-Aminocoumarin (2 g.) was treated with 25 c.c. of *N*-sodium carbonate solution, warmed to 60°, and ethyl chlorocarbonate (2·2 c.c.) slowly added with vigorous stirring. The straw-coloured, flocculent precipitate was filtered off, and crystallised from dilute alcohol, using animal charcoal, colourless rectangular plates being obtained (m.p. 156°) (yield 2·4 g.). (Found: C, 61·6; H, 4·8; N, 6·2. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7; N, 6·0 per cent.).

The coumarylurethane dissolves readily in alcohol, acetic acid, benzene and other common organic solvents. On heating for an hour to a temperature of 200° to 250°, symmetrical dicoumarylcarbamide was formed. The substance first melted and subsequently solidified to a light brown mass. The product was ground in a mortar, boiled repeatedly with alcohol, and the residue crystallised from nitrobenzene which deposited colourless crystals of the dicoumarylcarbamide (m.p. 326°).

The urethane was unaffected by boiling water, but on heating with water in a sealed tube at 180°—200° for three hours, a clear

solution was obtained from which, on cooling, crystals of aminocoumarin (m p. 165°) separated out. Similarly, although boiling concentrated hydrochloric acid failed to decompose the compound, it was quickly hydrolysed on heating with the acid in a sealed tube at 120°. The clear solution, on making alkaline with ammonia, precipitated yellow crystals of aminocoumarin.

Action of Aniline on Coumarylurethane.—No action occurred below 150°, the original substances being recovered unchanged at the end of three hours' heating. On using a little over a molecular proportion of aniline and maintaining the temperature at 200-220° for two hours, a dark mass was obtained from which, after repeatedly washing with hot alcohol and crystallising the residue from nitrobenzene, colourless crystals of dicoumarylcarbamide (m.p. 326°) were finally produced.

When a large excess of aniline (4 mols.) was employed and the temperature kept at 180-190°, a gray pasty mass was produced which after washing with dilute hydrochloric acid and crystallising twice from boiling alcohol using animal charcoal, formed sharp colourless needles melting at 236°. A mixed melting point determination with a pure sample of diphenylcarbamide showed them to be identical.

When equimolecular quantities of ethyl coumaryl-6-carbamate and 6-aminocoumarin were heated together at 200-220° for an hour and the product purified in the usual manner, crystals of dicoumarylcarbamide alone were obtained.

Besides the ethyl ester the following three alkyl coumarylcarbamates have been prepared by (*a*)condensing coumaryl 6-*iso*cyanate with the corresponding alcohol, and by (*b*) reacting 6-aminocoumarin with the corresponding chlorocarbonic ester:

Methyl Coumaryl-6-carbamate, m.p. 200-201°.
Propyl Coumaryl-6-carbamate, m.p. 129-130°.
iso*Butyl cupsoumaryl 6-carbamate*, m.p. 155-156°.

Phenyl Coumaryl-6-carbamate, $C_9H_5O_2{\cdot}NH{\cdot}CO_2Ph$.—Coumaryl *iso*cyanate was boiled with a slight excess of phenol in dry benzene for an hour. The benzene was distilled off, and the residue washed with weak alcohol to remove unchanged phenol. Crystallisation from hot alcohol gave colourless plates melting at 186-7°. (Found: N, 5·29. $C_{16}H_{11}O_4N$ requires N, 5·3 per cent.).

Symmetrical 6-dicoumarylcarbamide, $(C_9H_5O_5{\cdot}NH)_2CO$.—This has been prepared by the following methods:—

(*a*) A solution of 6-aminocoumarin (1 mol.) and coumaryl 6-*iso*cyanate (1 mol.) in dry benzene is boiled for a few minutes. The bulky precipitate is filtered, washed with dilute hydrochloric acid and with alcohol and finally crystallised from hot nitrobenzene.

(*b*) Carbonyl chloride (1 mol.) was mixed with 6-aminocoumarin (4 mols.) in benzene solution, the mixture allowed to remain at the ordinary temperature for an hour and finally boiled for half an hour. The precipitate consisting of a mixture of dicoumarylcarbamide and aminocoumarin hydrochloride was filtered, washed with boiling water and the residue dried and crystallised from nitrobenzene (m.p. 325°).

(*c*) Carbamide (1 mol.) and 6-aminocoumarin (2 mols.) were mixed with sufficient glacial acetic acid to form a clear solution, and the acid boiled off from a sand-bath till the whole turned into a viscous mass. This was collected, washed and crystallised in the usual way. (Found: N, 8·84. $C_{19}H_{12}O_5N_2$ requires N, 8·04 per cent.).

Coumaryl-6-carbamide, $C_9H_5O_2{\cdot}NH{\cdot}CO{\cdot}NH_2$.—It was prepared by the following methods:

(*a*) A current of dry ammonia was passed through a solution of coumaryl 6-*iso*cyanate in dry benzene and the reaction completed by allowing to stand for an hour. The bulky gelatinous precipitate was filtered and crystallised from alcohol; needles melting at 245°.

(*b*) 6-Aminocoumarin hydrochloride was dissolved in cold water, and the solution treated gradually with a slight excess of potassium cyanate. The precipitate was crystallised from hot glacial acetic acid which deposited colourless needles melting at 245° (decomp.). (Found: N, 13·8. $C_{10}H_8O_3N_2$ requires N, 13·72 per cent.).

The monocoumarylcarbamide solidified after melting, the product being found to be pure dicoumarylcarbamide.

Sym.-6-*coumarylphenylcarbamide*, $C_9H_5O_2{\cdot}NH{\cdot}CO{\cdot}NHPh$.—This was readily obtained as a crystalline precipitate on boiling a mixture of either coumaryl *iso*cyanate and aniline, or phenyl *iso*cyanate and aminocoumarin in dry benzene for a few minutes. Crystallisation from boiling alcohol gave colourless needles melting at 225-226°, with decomposition. (Found: N, 10·1 $C_{16}H_{12}O_3N_2$ requires N, 10·0 per cent.).

Coumarylphenylcarbamide (1 g.) was heated in a tube at 220°-240° for an hour; the solid melted, darkened in colour and then

solidified again. At the same time, colourless needles were found to have sublimed to the top of the tube which melted at 236°, and were identified as those of diphenylcarbamide. The dark residue at the bottom of the tube, after washing and crystallising from nitrobenzene, melted at 325°, and was proved to be dicoumarylcarbamide.

Phenyl-6-coumarylsemicarbazide, $PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_9H_5O_2$.—Coumaryl *iso*cyanate in dry benzene solution was treated with phenylhydrazine and then boiled for an hour. The separating solid was crystallised from boiling alcohol which deposited the semicarbazide as slender colourless needles melting at 236°. (Found: N, 14·48. $C_{16}H_{13}O_3N_3$ requires N, 14·23 per cent.).

Condensation of Coumaryl iso*Cyanate and Acetoxime*: *Formation of* $C_9H_5O_2{\cdot}NH{\cdot}CO_2{\cdot}N:C(Me)_2$.—Equivalent amounts of the *iso*cyanate and the oxime were boiled in benzene for an hour; the product crystallised on cooling as colourless hexagonal tablets melting at 187°. (Found: N, 10·89. $C_{13}H_{12}O_4N_2$ requires N, 10·77 per cent.).

4:7-*Dimethylcoumaryl* 6-iso*Cyanate*.—This was prepared from 4:7-dimethyl-6-aminocoumarin by the action of carbonyl chloride in the usual way. It crystallised from benzene as colourless stout needles melting at 215°. (Found: N, 6·86. $C_{12}H_9O_3N$ requires N, 6·51 per cent.).

Ethyl 4:7-*Dimethylcoumaryl-6-carbamate*, $(CH_3)_2C_9H_3O_2{\cdot}NH{\cdot}CO_2Et$.—This was obtained in two ways, *viz.*, (*a*) by boiling the *iso*cyanate with absolute alcohol, and (*b*) by treating a suspension of the aminocoumarin in warm sodium carbonate solution with ethyl chlorocarbonate. It separated from hot alcohol as colourless flat needles melting at 196°. (Found: N, 5·49. $C_{14}H_{15}O_4N$ requires N, 5·36 per cent.).

4:7-*Dimethylcoumaryl-6-carbamide*, $(CH_3)_2{\cdot}C_9H_3O_2{\cdot}NH{\cdot}CO{\cdot}NH_2$.—The gelatinous precipitate which came down on passing dry ammonia through a benzene solution of the *iso*cyanate was collected, washed with alcohol and crystallised from glacial acetic acid Colourless prisms were obtained melting at 250° (decomp.). The new product formed after decomposition melted at 328-330°, and was identified as di-4:7-dimethylcoumarylcarbamide. (Found: N, 12·37. $C_{12}H_{12}O_3N_2$ requires N, 12·07 per cent.).

Phenyl-4:7-dimethylcoumaryl -6- carbamide, $Me_2C_9H_3O_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}Ph$.—The same product was obtained by condensing either (*a*) 4:7-dimethylcoumaryl 6-*iso*cyanate with aniline, or (*b*) 6-amino-

4:7-dimethylcoumarin with phenyl *iso*cyanate. It formed needles from benzene melting at 265-266° (decomp.). (Found: N, 9·5. $C_{18}H_{16}O_3N_2$ requires N, 9·1 per cent.).

Di-(4:7-dimethyl)-6-coumarylcarbamide, $[Me_2C_9H_3O_2{\cdot}NH]_2CO$. —This was prepared by all the three different methods described in connection with dicoumarylcarbamide. It crystallised from nitrobenzene in colourless prisms melting at 320-330°. (Found: N, 7·2. $C_{23}H_{20}O_5N_2$ requires N, 6·93 per cent.).

PRESIDENCY COLLEGE, MADRAS.

Received March 24, 1931.

The Oil from the Seeds of *Putranjiva Roxburghii*, Wall.

By S. Krishna and S. V. Puntumbekar.

Putranjiva Roxburghii, Wall (N. O. *Euphorbiaceæ*; Vernacular —*Jiputa* or *Putranjiva*) is a moderate-sized evergreen tree with pendant branches, met wild and cultivated, throughout tropical India, from the lower Himalayas in Kumaon, eastwards and southwards, to Pegu and Ceylon. The leaves and stones of the fruit are officinal in certain parts of India and are given in decoction in colds and fevers. The seeds yield a pale yellow oil, which on standing deposits a small amount of solid matter and turns deeper in colour. "The stones of the fruit are strung together to form rosaries and hung round the necks of children to keep them in good health," hence the Sanskrit and the Vernacular names which signify 'the life of the child.' Hooper (Kirtikar and Basu, "Indian Medicinal Plants" p. 1148-49) records that in 1905 the seeds were tested in the Indian Museum and found to give 28·86% of the kernels and 42·9% of an oil in the kernels. But no data are given of the chemical examination of the oil.

Perusal of the literature shows that the oil, from putranjiva seeds, has never been examined carefully for its constituents and particularly for its active principles which are responsible for its supposed physiological effects. It was, therefore, considered a subject of interest and a chemical examination has now been made of the oil, as well as that of the pulp of the fruit, and the leaves. The oil has not shown any constituents, out of the ordinary, to which the physiological properties could be attributed. It is a glyceride of stearic, oleic, lignoceric and linoleic acids and is conspicuous by the total absence of palmitic acid. The pulp of the fruit, however, has been found to contain a large proportion of mannitol, a small quantity of a saponin glucoside, and a small quantity of an unidentified alkaloid.

Examination of the 'unsaponifiable matter' has shown it to contain sitosterol, which is unlikely to give the oil its therapeutic value. A small amount of a waxy matter, presumably a hydrocarbon of a high molecular weight, has also been separated from the unsaponifiable matter but its precise nature has not yet been identified. Tests for the presence of vitamines have also been made, both in the

oil and its unsaponifiable matter, and were found to be negative. From this it is concluded that the physiological activity of putranjiva, if at all there is any, is in all likelihood due to the glucoside and the alkaloid, a small quantity of which is also present in the stones of the fruit.

The putranjiva seeds used in this investigation were collected from trees in the Forest Research Institute, Dehra Dun.

Stones of the ripe fruit were collected, washed, dried and the kernels separated. The nuts contained 46 per cent. of kernels which in turn yielded 25% of the oil soluble in ether, the yield of crude oil was thus about 12% of the whole nut. The oil obtained by cold expression was of light pale yellow colour and clear in nature, but on standing for some weeks it deposited a fine curdy precipitate and also its colour deepened to an orange shade. A sample of the oil which was extracted in 1925 had turned deep orange in colour and its physical constants are noted below for purposes of comparison.

General Characteristics of the Oil.

	1930 oil.	1925 oil.
Consistency	Thin, clear	Thick, turbid due to sediment.
Colour	Pale yellow	Deep orange
Specific gravity at 30°/30°	0·9108	0·9283
Refractive index at 25°	1·4615	1·4623
Saponification value	189·9	198·50
Iodine value (Hanus)	93·8	79·49
Acetyl value	9·5	43·30
Hehner value	95·4	96·20
Unsaponifiable matter	0·75%	0·73%
Acid value	0·9	11·13

Composition of the Fatty Acids of Putranjiva Oil.

The fatty acids present in the kernels have been quantitatively investigated according to the customary methods of preliminary separation by the lead salt—alcohol method (Twitchell, *J. Ind. Eng. Chem.*, 1921, **13**, 806) into groups consisting respectively of mainly saturated and of mainly unsaturated acids, followed by conversion of each groups into methyl esters and systematic fractionation of the latter under vacuum. The results obtained are tabulated below. The liquid acids were found to consist chiefly of oleic (80%) and the linoleic (20%), while the solid acids consisted of stearic and

lignoceric. No attempt has been made to calculate the percentages of the solid acids as the nature of the intermediate products is not definitely known.

Chemical Constants of the Mixed Fatty Acids.

Mean molecular weight	...	...	292·5
Iodine value (Hanus)	...	...	101·9
Saturated acids (Twitchell's method)		...	21·4 per cent.
Unsaturated acids	...	...	77·6 per cent.

The crude fatty acids (389 g.) from 457 g. of the oil were treated with a slight excess of sodium hydroxide and the resultant soap was incorporated with filter paper pulp. The mass was dried, powdered and extracted with ether in a Soxhlet and the extract examined for unsaponifiable matter as described below.

Unsaturated Acids.

Methyl esters of the fatty acids were prepared in the usual manner (refluxing the acids with methyl alcoholic hydrochloric acid) and 85 g. of these were fractionated at 2 mm.

Fraction.	B.p.	Weight.	M.W. of the acids.	Iodine value.
L_1	50°–155°	1·28 g.	184·4	59·7
L_2	155°–165°	1·10	211·9	75·6
L_3	165°–170°	2·63	237·5	83·9
L_4	170°–175°	3·13	239·7	86·7
L_5	175°–176°	31·44	260·6	96·4
L_6	176°–177°	8·04	260·1	98·9
L_7	177°–180°	2·78	255·0	96·5
L_8	180°–183°	6·15	265·2	100·6
L_9	183°–185°	12·69	274·3	100·1
L_{10}	185°–195°	3·43	246·0	88·9
L_{11}	195°–210°	1·50	233·0	83·1
L_{12}	Residue	9·78		
Loss in distillation		1·10		
	Total	85·00 g.		

Of the above esters fractions L_5, L_6, L_7, L_8, and L_9 were mixed together and separately hydrolysed for further examination, the other fractions were left alone, being too small in amounts. The resulting soaps were oxidised with potassium permanganate in dilute cold solution and the hydroxy-acids obtained on neutralising the

mixture with sulphur dioxide were successively extracted with petroleum ether (b. p. 40-60°) to remove the unoxidised acids and the decomposition products. The residue, on extraction with ether, gave a product which on crystallisation from alcohol yielded an acid of M.W. 323 and m.p. 130-31°. These properties correspond very closely with those of dihydroxystearic acid. The residue, on further crystallisation, gave products melting over a wide range of temperature (155°-180°) but having molecular weight of the order of 348. This is not considered strange as many investigators (Power and Barrowcliff, *J. Chem. Soc.*, 1905, **87**, 899; Power and Moore, *J. Chem. Soc.*, 1910, **97**, 1103; Power and Salway, *J. Amer. Chem. Soc.*, 1910, **32**, 350; Tummin Katti and Puntambekar, *J. Indian Chem. Soc.*, 1930, **7**, 223) have found that acids agreeing in composition and character with tetrahydroxystearic acid possessed melting points varying from 156° to 178° and it is probable, therefore, that these compounds represent isomeric acids of the formula $C_{18}H_{36}O_6$. No hexahydroxystearic acid was found in the aqueous portion of the oxidised sodium soaps of the liquid acids.

A portion of the liquid acids on bromination (Lewkowitsch, "Chemical Technology & Analysis of Oils, Fats & Waxes," Vol. I, 6th edition, p. 585) gave no hexabromides. It, however, yielded a pale yellow product melting at 113-14° which was identified as tetrabromostearic acid by its mixed melting point with an authentic sample of tetrabromostearic acid.

The examination of the products of oxidation and bromination of the liquid acids, therefore, indicates in it the presence of oleic and linoleic acids, the former being 80% and the latter 20% of the liquid acids.

Saturated Acids.

The methyl esters (62 g.) of these acids on fractional distillation under a pressure of 2 mm. gave the following fractions:

Fraction.	B. p.	Weight.	M. W. of the acids.
S_1	Up to 162°	1·04 g.	247·0
S_2	162°–167°	4·24	257·4
S_3	167°–171°	2·71	260·3
S_4	171°–173°	23·93	264·4
S_5	173°–176°	6·31	267·3
S_6	176°–177°	5·30	272·9
S_7	177°–179°	5·94	280·2
S_8	179°–181°	3·06	282·7
S_9	181°–185°	2·58	290·1
S_{10}	185°–200°	3·34	312·4
S_{11}	Above 200°	3·00	
	Loss in distillation	0·55	
		62·00 g.	

The acids liberated from each of the fractions were subjected to fractional crystallisation to identify the individual acids.

Fraction S_1.—Crystallisation from dilute alcohol gave a product of m.p. 67-68° and M. W. 283. It was identified as stearic acid on taking a mixed melting point with an authentic sample.

Fraction S_2 yielded a saturated acid of m.p. 68-69° (unchanged when mixed with stearic acid) and M.W. 315. The filtrate from the above yielded a product, m.p. 56-57° and M.W. 274. The residue had a M.W. of 315.

Fraction S_3.—After several crystallisations it yielded a product, m.p. 60-68° and M.W. 284 ; mixed m.p. with pure stearic acid was slightly higher, consequently appeared to be impure stearic acid. The residue from the filtrate, on concentration and crystallisation gave a M.W. 238.

Fraction S_4 gave an acid melting at 68-69° (unchanged when mixed with stearic acid). The mother-liquor on further concentrations gave a material melting at 54° and M.W. 292·6. The final residue had M.W. 376.

Fraction S_5.—On crystallisation from alcohol the acid melted at 68-69° and had M.W. 288 ; identified as stearic acid. The residue on concentration and crystallisation gave a substance of M.W. 378.

Fraction S_6 gave an acid m. p. 67·5-68·5° and M. W. 286 ; identified as stearic acid. The filtrate gave two products of M.W's. 328 and 346 respectively.

Fraction S_7 gave a product melting at 68-69° (not depressed when mixed with pure stearic acid). From the filtrate two products were obtained having M.W's. 354 and 396 respectively.

Fraction S_8.—From this fraction stearic acid was isolated and identified as above. The filtrate gave products having M. W's. 313 and 339 respectively.

Fraction S_9.—No definite acid could be isolated from this fraction. The crystalline product obtained had a m.p. 62-63·5° and M.W. 296·5, indicating it to be impure stearic acid. On crystallisation of the filtrates a residue of M.W. 337 was obtained.

Fraction S_{10} gave no definite acid. The product after several crystallisations from alcohol melted at 61-63° and M.W. 304·8. The filtrate on further concentrations and crystallisation yielded products of M.W. 396 and 318.

Fraction S_{11} gave an acid of m.p. 77·5-78·5° and M.W. 370. Its mixed melting point with lignoceric acid remained unaltered.

The filtrate residue consisted mainly of the colouring matters and decomposition products.

The residues from the filtrate of the Fractions S_2—S_{11} were combined together and crystallised from alcohol, when a colourless crystalline product of m.p. 59-61° and M.W. 284 was obtained, and it appeared to be impure stearic acid. The filtrate on further concentration and crystallisation gave an acid of M.W. 348·5. The residue obtained had a M.W. 454 and m.p. below 55°. The acids (M.W. 348·5 and 454), on further examination were found to be mixtures of esters and free acids both of which on hydrolysis yieided an acid of M.W. 282, which presumably is stearic acid.

Unsaponifiable Matter.

The unsaponifiable matter after several crystallisations from rectified spirit gave a white crystalline product m.p. 143-145° and gave all the characteristic tests of phytosterol. The acetyl derivative after crystallisation melted at 129-130°. This phytosterol has been identified as sitosterol.

A small amount of a waxy material presumably a hydrocarbon of high molecular weight, insoluble in concentrated sulphuric acid was also obtained from the unsaponifiable matter but the amount was too small for identification purposes.

Summary.

The oil from the seeds of *Putranjiva Roxburghii* has been found to contain the glycerides of stearic, lignoceric, oleic and linoleic acids together with sitosterol melting at 143-145°. The presence of palmitic acid has not been detected.

FOREST RESEARCH INSTITUTE, DEHRA DUN. *Received March* 30, 1931.

A Note on the Constitution and Isomerism of Thiosulphuric Acid.

By Priyadaranjan Rây.

It is well known that the constitution of thiosulphuric acid may be represented in two different ways as given by formulae I and II:—

I II

The formula I accounts for the formation of its salts from sulphites and sulphur and for the decomposition of the acid into sulphurous acid and sulphur. On the other hand, the decomposition of heavy metal thiosulphates in presence of water by heat into sulphide and sulphuric acid, the formation of sodium alkylthiosulphate and its decomposition by acids into mercaptan and sulphate as well as its oxidation by nitric acid to alkylsulphonic acid and sulphuric acid speak strongly in favour of the second formula.

That the thiosulphates are decomposed by acids under certain circumstances with liberation of hydrogen sulphide was already observed by Colson (*Bull. Soc. chim.*, 1880, [2], **34**, 66), Vaubel (*Ber.*, 1889, **22**, 1686) and Vortmann (*Ber.*, 1889, **22**, 2307); (*cf.* Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1401; Foerster, *Z. anorg. Chem.*, 1928, **177**, 61).

Further Piccard and Thomas (*Helv. Chim. Acta*, 1923, **6**, 1032), have shown that sulphur trioxide and hydrogen sulphide dissolved in liquid carbon dioxide at $-50°$, when cooled to liquid air temperature, combine with each other. The authors concluded from this that they succeeded in synthesising the veritable thiosulphuric acid $SO_3 \cdot SH_2$, corresponding to the formula II.

Very convincing evidence regarding the existence of two isomeric forms has been obtained in this laboratory and the two modifications

as constituents of a complex acid have actually been isolated. When preparing the complex thiosulphate-pentacyanocobaltic acid $H_4[(CN)_5 \cdot Co \cdot S_2O_3]$, whose potassium salt was described in this Journal (Rây, *J. Indian Chem. Soc.*, 1927, **4**, 325), from its basic lead salt by decomposition with hydrogen sulphide, it was observed that the solution of the complex acid thus obtained differed in its behaviour from that of the solid acid prepared by evaporating the above solution in *vacuo* over sulphuric acid.

The solution of the complex acid freshly prepared from the lead salt was *yellow to orange in colour* according to concentration. It hydrolysed on heating and the thiosulphuric acid liberated thereby decomposed into sulphurous acid and sulphur.

$$H_4[(CN)_5 \cdot Co \cdot O \cdot S_2O_2] + H_2O \longrightarrow H_2[(CN)_5 \cdot Co \cdot OH_2] + HO \cdot SO \cdot OH \;(\Vert\, S) \downarrow \; H_2SO_3 + S$$

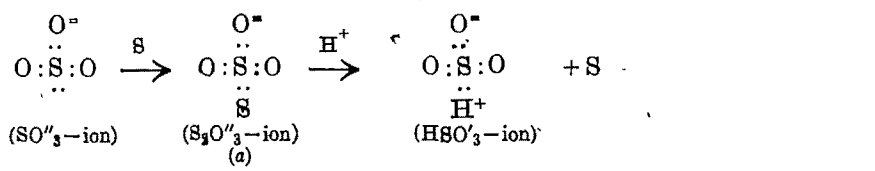
The potassium salt of this acid when heated with mineral acids in aqueous solution decomposed in a similar manner. Barium and calcium salts prepared by neutralisation of the aqueous solution of the acid, thus obtained, with their carbonates also underwent similar decomposition. On the other hand, the *orange red crystals* of the solid acid prepared from the above solution dissolved in water with *yellow to orange colour* with separation of a little sulphur and gave out hydrogen sulphide. On warming, the colour of the solution became *dark red* with increased evolution of H_2S gas. Sulphuric acid was formed in the solution. The solution did not yield any sulphur dioxide even on boiling. This evidently indicates a change in the structure of the complex acid during solidification whereby a change in the mode of linking of the thiosulphate S_2O_3 radical to the central cobalt atom occurs, and the thiosulphuric acid liberated from the latter (solid acid) by hydrolysis consequently presents a different structure.

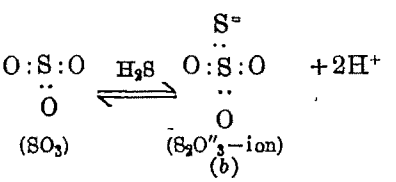
$$H_4[(CN)_5 \cdot Co\ S\ SO_3] + H_2O \longrightarrow H_2[(CN)_5 \cdot Co \cdot OH_2] + HS \cdot SO_2 \cdot OH \downarrow \; H_2S + SO_3$$

The separation of a little sulphur that was observed when the solid acid dissolved in water was evidently due to the interaction between H_2S and SO_3 in the solid acid itself as the result of slight decomposition.

Further, the solution of the solid acid when neutralised with magnesium, calcium and ammonium carbonates gave *reddish brown salts*, which on treatment with mineral acids, evolved hydrogen sulphide and no sulphur dioxide. This proves beyond doubt that the complex acid exists in two isomeric modifications. The change is however an irreversible one, since the solid acid or its solution has not yet been found to change so as to give rise to the modification that exists in the original solution.

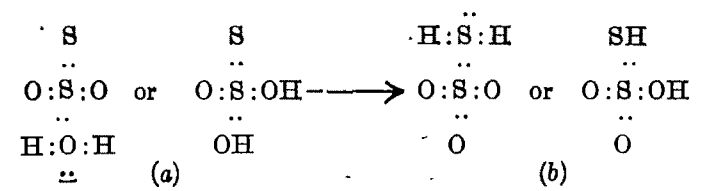
Judging by analogy, it may therefore be stated that the two varieties of thiosulphuric acid resulting from the hydrolysis of the two isomeric complex acids also present a case of irreversible change or true isomerism. In the light of the modern electronic theory of valency, the constitution and behaviour of the two modifications of thiosulphuric acid and the nature of the isomerism can be readily explained as shown below by forms (*a*) and (*b*).





The form (*a*) corresponds to the usual decomposition of thiosulphuric acid whereas (*b*) suggests that it can be formed by the condensation of hydrogen sulphide with sulphur trioxide just as the latter gives sulphuric acid with water. On decomposition, it should therefore give, on the assumption that no rearrangement occurs, hydrogen sulphide and sulphur trioxide or sulphuric acid. The course of decomposition in both cases is peculiarly alike consisting in the separation of a sulphur atom from the complex anion S_2O_3, only with this difference that in the first case (*a*) it is dropped as elementary sulphur whereas in the second case (*b*) the sulphur leaves as a sulphide ion, which then combines with hydrogen ions to form hydrogen sulphide. In the ionic condition there is apparently little difference in the constitution of the two forms. It is only in the location of the charge in the complex $[S_2O_3]$ ion that a distinction could be detected. Conse-

quently the irreversible change of the first modification into the second consists in the transfer of charge from the co-ordinated oxygen to the co-ordinated sulphur atom by shifting of the electron pairs linking these atoms with the central sulphur atom. In the non-ionised form the change can be represented in a much clearer manner by the mobility of hydrogen atoms.



The two modifications of thiosulphuric acid corresponding to the forms (*a*) and (*b*) may be termed α-and β-thiosulphuric acids and the phenomenon as one of "electro-isomerism."

The conception of Werner that once an ion enters a co-ordination complex its hold upon the charge is weakened and the latter is distributed uniformly over the complex or is concentrated on the central atom seems however irreconciliable with the present knowledge. Presumably a neutral atom or an ion of the same cannot be held by the central atom with the same intensity of force. In some cases however a redistribution may indeed occur inside the complex after the combination has taken place.

Analytical results and other experimental details regarding the preparation and properties of the two isomeric complex thiosulphatopentacyanocobaltic acids as well as of their various salts will be published hereafter.

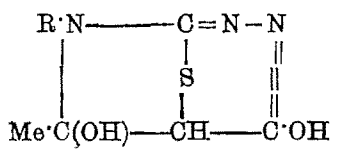
CHEMICAL LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

Received February 26, 1931.

Thiodiazines. Part VIII. Action of Ethyl α-Chloroacetoacetate upon Thiosemicarbazides.

By Prafulla Kumar Bose and Birendra Kumar Nandi.

The interaction of 4-substituted thiosemicarbazides and ethyl α-chloroacetoacetate leads to the formation of well defined crystalline products, having the general formula, $R{\cdot}C_5H_6O_2N_3S$ showing that the ester grouping takes part in the condensation. This is rather remarkable in view of the fact that the keto-group of the ester takes part in ring formation when thiocarbamide is employed (Zürcher, *Annalen*, 1889, **250**, 281). The products were found to be insoluble in sodium carbonate but soluble in alkali. They yielded well defined hydrochlorides and acetyl derivatives; the latter were insoluble in alkali and could be easily de-acetylated to the original substances by the action of aqueous-alcoholic hydrochloric acid. They failed to condense with phenylhydrazine or semicarbazide under the usual conditions. Moreover, they could not be made to condense with aldehydes or ketones. They did not impart any characteristic coloration to ferric chloride. These facts suggest the following formula as a possible structure for these condensation products.



Experimental.

4-Methylthiosemicarbazide and Ethyl α-Chloroacetoacetate.—4-Methylthiosemicarbazide (3 g.) was dissolved in 50 c.c. of dry absolute alcohol and ethyl α-chloroacetoacetate (4·7 g.) was added and the mixture shaken for half an hour. Reaction took place with evolution of heat. The whole was then refluxed for about

20 minutes on the water-bath to complete the reaction. On evaporation of the solvent at the ordinary temperature, yellowish crystals separated out. These were collected and dried over porous plate (2·6 g.). The free base was then isolated by extracting the product with hot 5—7% hydrochloric acid and then treating the extract with a very dilute solution of sodium carbonate. The colourless crystals (1·8 g.) thus obtained were recrystallised from alcohol in needles, m. p. 156°. The base dissolved in hot aqueous alkali. (Found: C, 38·68; H, 4·99; N, 22·27. $C_6H_9O_2N_3S$ requires C, 38·50; H, 4·81; N, 22·44 per cent.). It is soluble in acetic acid, and acetone, sparingly in benzene and insoluble in chloroform and ether.

The *acetyl* derivative, crystallised in long colourless needles melting at 65°. It is insoluble in aqueous alkali. (Found: N, 18·51. $C_8H_{11}O_3N_3S$ requires N, 18·34 per cent.). The *hydrochloride* separated from alcohol in colourless needles, m. p. 197°. (Found: Cl, 15·6. $C_6H_{10}O_2N_3SCl$ requires Cl, 15·88 per cent.).

4-iso*Butylthiosemicarbazide and Ethyl α-Chloroacetoacetate.*—The procedure was identical. The base crystallised from alcohol in colourless needles melting at 145°. (Found: C, 47·26; H, 6·39; N, 18·18. $C_9H_{15}O_2N_3S$ requires C, 47·11 ; H, 6·55 ; N, 18·34 per cent.).

The *hydrochloride* melted at 158°. The *acetyl* derivative crystallised from methyl alcohol (needles), m. p. 240°. (Found: C, 48·51; H, 6·89; N, 15·61. $C_{11}H_{17}O_3N_3S$ requires C, 48·70; H, 6·27; N, 15·49 per cent.).

4-*Phenylthiosemicarbazide and Ethyl α-Chloroacetoacetate.*—Prepared in the usual manner it crystallised from alcohol in colourless needles melting at 166°. It is also soluble in chloroform and ether. (Found: C, 53·5; H, 4·7; N, 16·89. $C_{11}H_{11}O_2N_3S$ requires C, 52·9; H, 4·4; N, 16·86 per cent.).

The *hydrochloride* crystallised from alcohol, m.p. 149°. (Found: N, 14·9. $C_{11}H_{12}O_2N_3SCl$ requires N, 14·71 per cent.). The *acetyl* derivative formed almost colourless needles, m.p. 118°. (Found: C, 53·88; H, 4·67; N, 14·70. $C_{13}H_{13}O_3N_3S$ requires C, 53·69; H, 4·47; N, 14·4 per cent.).

Hydrolysis.—One g. of the acetyl derivative was dissolved in aqueous alcohol and refluxed on the water-bath after the addition of an excess of hydrochloric acid. On cooling the solution was diluted and made alkaline with sodium carbonate. The free base

was collected and on crystallisation from alcohol melted at 166° alone or when mixed with the above phenyl compound.

4-o-*Tolylthiosemicarbazide and Ethyl α-Chloroacetoacetate*.—The condensation product was obtained as usual. It was finally crystallised from alcohol in beautiful, long needles, m. p. 165°. (Found: N, 15·87. $C_{12}H_{13}O_2N_3S$ requires N, 15·97 per cent.)

The *acetyl* derivative formed colourless plates from alcohol, m. p. 175°. (Found: N, 13·58. $C_{14}H_{15}O_3N_3S$ requires N, 13·77 per cent.). The *hydrochloride* crystallised from alcohol in silky needles melting at 147°.

4-p-*Tolylthiosemicarbazide and Ethyl α-Chloroacetoacetate*.—The product formed slender needles from alcohol, m. p. 181°. (Found: N, 16·07. $C_{12}H_{13}O_2N_3S$ requires N, 15·97 per cent).

The *acetyl* derivative crystallised from absolute alcohol in colourless needles melting at 124°. (Found: C, 55·18; H, 5·20; N, 13·49. $C_{14}H_{15}O_3N_3S$ requires C, 55·08; H, 4·91; N, 13·77 per cent.).

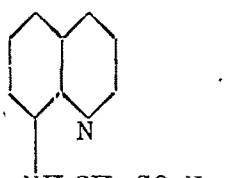
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
CALCUTTA.

Received April 27, 1931.

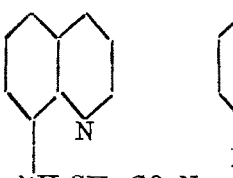
Studies in Quinoline Compounds. Part IV,

By Upendra Nath Brahmachari, Jnanendra Mohan Das-Gupta and Tarapada Bhattacharjee.

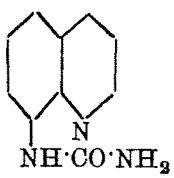
The present paper deals with certain new quinoline derivatives which, from theoretical considerations, may be of therapeutic interest.



(I)



(II)



(III)

The following are the series of compounds described in the present paper:

1. Sodium 8-aminoquinoline-*N*-methylenesulphonate (I).
2. ,, 6-aminoquinoline-*N*-methylenesulphonate.
3. ,, 6-methoxy-8-aminoquinoline-*N*-methylenesulphonate.
4. ,, 8-aminoquinoline-*N*-methylenesulphinate (II).
5. ,, 6-aminoquinoline-*N*-methylenesulphinate.
6. ,, 6-methoxy-8-aminoquinoline-*N*-methylenesulphinate.
7. 8-Carbamidoquinoline (III).
8. 6-Carbamidoquinoline.
9. 6-Methoxy-8-carbamidoquinoline.

These have been prepared by the replacement of one hydrogen atom of the amino-group in 6-aminoquinoline, 8-aminoquinoline and 6-methoxy-8-aminoquinoline by (*i*) $CH_2 \cdot SO_3Na$ (*ii*) $CH_2 \cdot SO_2Na$ and (*iii*) $CO \cdot NH_2$ groups. In the last instance compounds having $\cdot NH \cdot CO$. group have been obtained which play an important part in therapeutic action in compounds such as tryparsamide, urea stibamine, antimony analogue of tryparsamide, Bayer 205, Fourneau 309, etc.

Experimental.

Sodium 8-Aminoquinoline-N-methylenesulphonate.—A solution of 8-aminoquinoline hydrochloride (2 g.) in 5 c.c. of water, containing alcohol (2 c.c.) is treated successively with formaldehyde (1·2 c.c. of 30%) and sodium bisulphite (2 g.) freshly dissolved in water (5 c.c.) and the whole warmed on a water-bath for ½—1 hour. The precipitated base gradually dissolves when a reddish solution is obtained. It is then filtered and the clear filtrate concentrated on water-bath and then precipitated by means of absolute alcohol. It crystallises in long yellow needles; does not melt but dissolves readily in water to a neutral solution. (Found: N, 12·0. $C_{10}H_9O_3N_2Na$ requires N, 12·3 per cent.).

Sodium 6-Aminoquinoline-N-methylenesulphonate.—6-Aminoquinoline hydrochloride (1·5 g.) is treated similarly with 1 c.c. of formaldehyde and sodium bisulphite (1·5 g.) in aqueous solution. The product is obtained as reddish-brown needles after precipitation with absolute alcohol. The compound does not melt. (Found: N, 12·1. $C_{10}H_9O_3N_2Na$ requires N, 12·3 per cent.).

Sodium 6-Methoxy-8-aminoquinoline-N-methylenesulphonate.—6-Methoxy-8-aminoquinoline hydrochloride when treated as above gives the sodium salt of 6-methoxy-8-aminoquinoline-*N*-methylenesulphonic acid. The former (1 g.) is dissolved in 5 c.c. of water and the solution is then warmed for sometime with 1 c.c. of formaldehyde solution and 3 c.c. of 40% sodium bisulphite solution. The solution after filtration yields the final product by precipitating with alcohol or acetone. It is a reddish-yellow compound, crystallising in needles which do not melt. (Found: N, 10·7. $C_{11}H_{11}O_4N_2Na$ requires N, 10·85 per cent.).

Sodium 8-Aminoquinoline-N-methylenesulphinate.—8-Aminoquinoline dissolved in 10 c.c. of water is treated with an excess of sodium formaldehyde sulphoxylate in concentrated aqueous solution and warmed on a water-bath for ½—1 hour. The solution is filtered and the clear filtrate precipitated by acetone or alcohol when yellow needles are obtained. The needles do not melt below 300° but dissolve readily in water. (Found: N, 13·1. $C_{10}H_9O_2N_2Na$ requires N, 13·2 per cent.).

Sodium 6-Aminoquinoline-N-methylenesulphinate.—The 6-aminoquinoline derivative is obtained in a similar way by the action of an excess of sodium formaldehyde sulphoxylate preferably in presence

of alcohol (ethyl or methyl). It is a reddish-yellow compound which shows no melting point. (Found: N, 13·0. $C_{10}H_9O_2N_2Na$ requires N, 13·2 per cent.).

Sodium 6-Methoxy-8-aminoquinoline-N-methylenesulphinate.—6-Methoxy-8-aminoquinoline hydrochloride (1 g.) is dissolved in 3 c.c. of water and 1 c.c. of alcohol. Approximately 2 g. of sodium formaldehyde sulphoxylate in concentrated aqueous solution are added and the mixture warmed for sometime. The solution after filtration and precipitation with alcohol gives the final product in a crystalline form. It does not melt below 300°. (Found: N, 11·3. $C_{11}H_{11}O_3N_2Na$ requires N, 11·54 per cent.).

8-Carbamidoquinoline or Quinoline-8-carbamide.—This compound is obtained by heating 8-aminoquinoline and carbamide in equimolecular proportions in an oil-bath at 170° for about an hour. It is then treated with water and filtered. The precipitate is recrystallised from absolute alcohol. At the beginning we expected that we would get from this reaction a compound of the type of diquinolylcarbamide but we found after analysis that the compound was a carbamido-derivative. This compound is identical with the one obtained from 8-aminoquinoline hydrochloride and potassium cyanate in the usual way. It crystallises in brownish-white microscopic needles, easily soluble in dilute acids, insoluble in ether, acetone or water. It melts with slight decomposition at 206°. (Found: N, 22·2. $C_{10}H_9ON_3$ requires N, 22·4 per cent.).

6-Carbamidoquinoline.—It is prepared similarly as above, from 6-aminoquinoline and carbamide. It can also be obtained from 6-aminoquinoline hydrochloride and potassium cyanate. It melts at 208°, easily soluble in alcohol, moderately so in acetone, and insoluble in ether or water. (Found: N, 22·1. $C_{10}H_9ON_3$ requires N, 22·4 per cent.).

6-Methoxy-8-carbamidoquinoline was obtained as above from either potassium cyanate and 6-methoxy-8-aminoquinoline hydrochloride or 6-methoxy-8-aminoquinoline and carbamide. It melts at 218°. (Found: N, 19·0. $C_{11}H_{11}O_2N_3$ requires N, 19·3 per cent.).

Observations on toxicity, pharmacological action and therapeutic properties of the above compounds are in progress.

THE BRAHMACHARI RESEARCH INSTITUTE,
82/3 CORNWALLIS STREET, CALCUTTA.

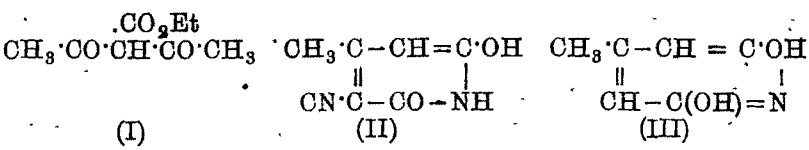
Received April 11, 1931.

β-Diketones in Ring Formation, Part IV.

By Umaprasanna Basu.

Ascertaining certain factors which govern the course of reaction between a substance containing a reactive methylene group, such as cyanoacetamide, and an αγ-dicarbonyl compound (Basu, *J. Indian Chem. Soc.*, 1930, **7**, 481, 815), it was now found necessary to have also an idea of the influence of a negative substituent, CO_2Et, CO·R etc., at the methylene carbon atom of the dicarbonyl compound on the course of this reaction.

Accordingly ethyl diacetoacetate (I) was treated with cyanoacetamide in dilute alcoholic solution in presence of a little piperidine when no condensation product separated after 3 or 4 days. On acidifying the solution however even after a day, a product was isolated which unlike the pyridone derivative previously synthesised (Basu, *loc. cit.*), easily dissolved in sodium carbonate solution with effervescence and gave a characteristic coloration with alcoholic ferric chloride. It had the formula $C_7H_6O_2N_2$ and was identified as 2-keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine (II) by its hydrolysis to the known 4-methyl-2:6-dihydroxypyridine (III) (Rogerson and Thorpe, *J. Chem. Soc.*, 1905, **87**, 1688) and by its synthesis from cyanoacetamide and ethyl acetoacetate (*cf.* Guareschi, *R. Accad. Sci. Torino.*, *Chem. Zentr.*, 1896, **1**, 602; 1896, II, 46). It becomes evident that during condensation one of the acetyl groups of ethyl diacetoacetate was eliminated as was also perceived from a distinct smell of ethyl acetate in the reaction mixture. This occurred even when the reaction was conducted at 0° or with cyanoacetmethylamide when *N*-methyl derivative of 2-keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine (II) was easily isolated.

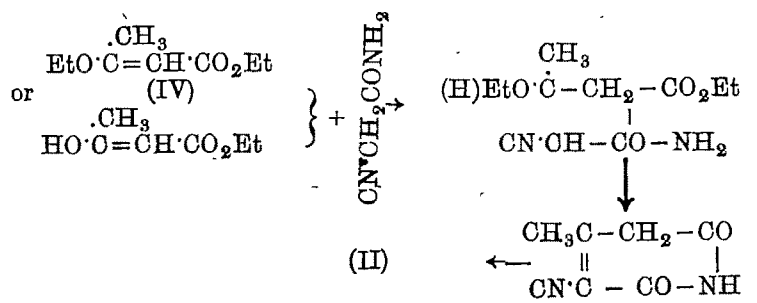


(I) (II) (III)

The question now arises whether in the reaction with such dicarbonyl compounds, ethyl diacetoacetate, ethyl acetoacetate (β-ketonic

esters), the ethylenic linkage formed by the enolisation of the keto-group is responsible for the initial condensation or the carbonyl group remaining as such, becomes the centre of reaction Thorpe and Rogerson (*loc. cit.*), and Thorpe (*Proc. Chem. Soc.*, 1912, p. 51) are of opinion that ethyl cyanoacetate preferentially reacts with the enolic form of ethyl acetoacetate to give rise to a glutaconic ester derivative. Similarly cyanoacetamide might have reacted with the enolic form of acetoacetic ester or diacetoacetic ester to give rise to the same (by the elimination of an acetyl group in the latter case) pyridone derivative.

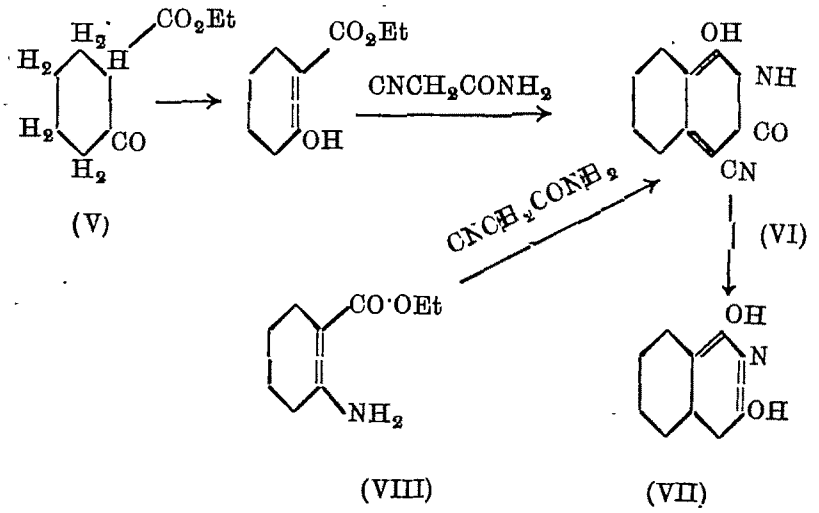
So ethyl ethoxycrotonate (IV), an *O*-ether of ethyl acetoacetate in which the ethylenic bond is fixed, was prepared and its reaction with cyanoacetamide studied, when 2-keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine (II), m.p. 304° (decomp.) was easily isolated. The formation of this may now be represented in the following way:—

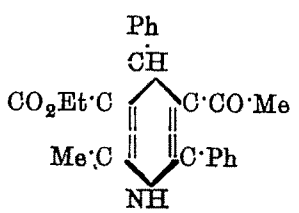


Similarly ethyl β-aminocrotonate (X) when heated with cyanoacetamide afforded 2-keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine.

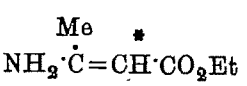
Next a cyclic β-ketonic ester, ethyl *cyclo*hexanone-2-carboxylate (V) was condensed with cyanoacetamide to synthesise 3-keto-4-cyano-1-hydroxy-2:3:5:6:7:8-hexahydro*iso*quinoline (VI) which on hydrolysis with hydrochloric acid gave 1:3-dihydroxy-5:6:7:8-tetrahydro*iso*quinoline (VII). The *iso*quinoline derivative (VI) was also obtained when ethyl tetrahydroanthranilate (VIII) was heated with cyanoacetamide under the experimental conditions described later. The tetrahydroanthranilate did not undergo any appreciable decomposition when heated alone under the same experimental conditions and afforded no condensation product when treated with benzal benzoylacetone, $Ph{\cdot}CH{=}C(CO{\cdot}CH_3){\cdot}CO{\cdot}Ph$. A similar mixture of the latter and ethyl β-aminocrotonate gives a crystalline product (IX) as found by Knoevenagel (*Ber.*, 1903, **36**, 2188). The inactivity of

the ethyl tetrahydroanthranilate shows that the presence of a labile methine hydrogen atom* as present in the β-aminocroto nic ester (X) is essential for the above reaction or in other words the β-ketonic ester derivatives react in the form (VIII) or (X) in the condensation reaction (*cf.* also Perkin, *J. Chem. Soc.*, 1892, **61**, 835). This again points to the preferential addition of the methylene group to the ethylenic linkage present in systems as represented above, in this type of reaction.





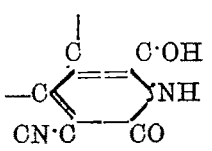
(IX)



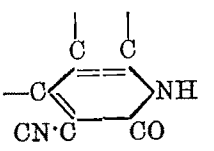
(X)

The compounds described in this paper react in accordance with the formula (XI) and thereby it is in agreement with that of the pyridone derivative (XII) obtained by condensing a β-diketone with cyanoacetamide (Basu, *loc. cit.*), the only difference being that the former (XI) contains a hydroxyl group, the presence of which increases the acidity of these compounds even in the *N*-methyl derivatives whereas the corresponding derivatives of (XII) are not soluble even in caustic alkali. The above condensation products have thus been described as ketohydroxy derivatives.

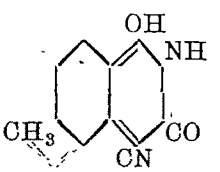
In Part III of this series (*J. Indian Chem. Soc.*, 1931, **8**, 119) it has been shown that *p*-toluoylacetoneamine $CH_3 \cdot C_6H_4 \cdot CO \cdot CH^* = C(CH_3) \cdot NH_2$ when heated with cyanoacetamine gave 3-cyano-4-methyl-6-*p*-tolyl-2-pyridone identical with that obtained from *p*-toluoylacetone itself. Here it has been found that benzoylacetone amine $Ph \cdot CO \cdot \overset{*}{C}H = C(CH_3) \cdot NH_2$ (Fischer and Bülow, *Ber.*, 1885, **18**, 2134 ; Claisen, *Ber.*, 1926, **59**, 144) similarly afforded 3-cyano-4-methyl-6-phenyl-2-pyridone, m. p. 310°, (Basu, *loc. cit.*). This on methylation gave 3-cyano-1 : 4-dimethyl-6-phenyl-2-pyridone, m. p. 265°, which on hydrolysis with concentrated hydrochloric acid was converted into 1 : 4-dimethyl-6-phenyl-2-pyridone isolated in the form of its hydrochloride, the free base being an oil soluble in ether but giving no sharp coloration to alcoholic ferric chloride. Benzoylacetoneamine has also been found to react with benzalbenzoylacetone by Knoevenagel (*loc. cit.*). But from a similar experiment with an amine, $CH_3 \cdot CO\ C(Me) = C(Me) \cdot NH_2$ prepared from methylacetylacetone where there is no methine hydrogen atom, no definite condensation product was isolated, whereas *p*-toluoylacetoneamine gave, when heated with benzalbenzoylacetone, 2-methyl-4 : 6-diphenyl-3-*p*-toluoyl-5-acetyl-1 : 4-dihydropyridine (XIII), m. p. 183°, as a yellow crystalline solid. Further work with dicarbonyl compounds containing the substituent at the methylene carbon atom is in progress.



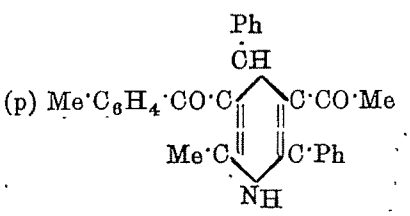
(XI)



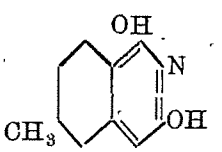
(XII)



(XIV)



(XIII)



(XV)

EXPERIMENTAL.

Ethyl Diacetoacetate and Cyanoacetamide: Formation of 2-Keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine.—The ester was prepared according to Claisen and Zedel (*Annalen*, 1893, 277, 175) and obtained as a colourless liquid, b. p. 82°/6 mm. The copper salt melted at 150-51°. Cyanoacetamide (4·2 g.) was dissolved in water by warming and the ester (8·6 g.) added, with just enough alcohol to effect the solution. The solution was then warmed at about 50° with the addition of piperidine (2 c.c.) but no crystal separated out even after 6 hours. Smell of ethyl acetate was distinctly perceived in the reaction mixture when a further quantity of piperidine (1 c.c) being added it was left overnight. The clear solution on acidification with dilute hydrochloric acid gave a crystalline solid (3·6 g.). On crystallisation from boiling water it melted at 304° with decomposition sintering earlier. (Found: C, 55·57; H, 4·31; N, 18·45. $C_7H_6O_2N_2$ requires C, 56·0; H, 4·0; N, 18·67 per cent.).

The compound is soluble in boiling water, alcohol and acetic acid. It dissolves in alkali and in alkaline carbonate with effervescence and gives with alcoholic ferric chloride a deep bluish-violet and with sodium nitrite solution a bluish-green coloration. The substance was heated with the concentrated acid at 150-60° for about 4 hours in a sealed tube and the acid product was made alkaline with ammonia and slowly neutralised with acetic acid when crystals that separated were collected and on crystallisation from dilute alcohol melted at 194°. (Found: N, 10·96. $C_6H_7O_2N$ requires N, 11·2 per cent,). It also dissolves in sodium carbonate solution with effervescence, gives with sodium nitrite solution a blue coloration and with alcoholic ferric chloride a reddish-violet coloration disappearing on warming, and possesses all the characteristics ascribed to 4-methyl-2: 6-dihydroxypyridine (III) by Rogerson and Thorpe (*loc. cit.*). The mother compound was then found to be 2-keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine (II) and as further proved by its synthesis from ethyl acetoacetate and cyanoacetamide (*vide infra*).

Ethyl Diacetoacetate and Cyanoacetmethylamide: Formation of 2-Keto-3-cyano-1: 4-dimethyl-6-hydroxy-1: 2-dihydropyridine (II, NH=NCH$_3$).—The condensation was effected as usual by means of piperidine and the product isolated after 2 days on acidification, crystallised from boiling water in clusters of needles, m.p. 274°,

(Found: N, 17·01. $C_8H_8O_2N_2$ requires N, 17·07 per cent.). It dissolves in sodium carbonate solution with effervescence, gives with sodium nitrite solution a green coloration and with ferric chloride a bluish-violet coloration which disappears on slight warming.

Condensation of Cyanoacetamide with Ethyl Acetoacetate and its Derivatives.

(*i*) The condensation between cyanoacetamide and ethyl acetoacetate was brought about in the usual way. The yield was only 35-40 per cent. On crystallisation from boiling water the product melted at 304° (decomp). The compound, 2-keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine, has been already studied by Guareschi (*loc. cit.*).

(*ii*) *With Ethyl Ethoxycrotonate* (IV).—The *O*-ether of acetoacetic ester was prepared according to Claisen's method (*Ber.*, 1893, **26**, 2731) and its condensation with sodiocyanoacetamide was effected exactly in the same way as in the case of other ethers similarly studied (Basu, *loc. cit.*). After 3 days water was added to have a clear solution. It was then extracted with ether. The ethereal solution on evaporation gave the unreacted ethyl ethoxycrotonate in its pure form in more than half the quantity used in the condensation. The aqueous solution on acidification afforded 2-keto-3-cyano-4-methyl-6-hydroxy-1:2-dihydropyridine (yield about 35 per cent.). On crystallisation from boiling water it melted at 304° (decomp). (Found: N, 18·52. $C_7H_6O_2N_2$ requires N, 18·67 per cent.). The condensation might also be brought about in presence of piperidine.

(*iii*) *With Ethyl β-Aminocrotonate.*—Molecular quantities of cyanoacetamide and ethyl β-aminocrotonate were heated at 130° on an oil-bath for about 15 minutes, when the usual condensation product was isolated in the form of its ammonium salt from which dilute hydrochloric acid liberated the free pyridine derivative melting at the same temperature when mixed with the product just described above.

Ethyl cyclo*Hexanone-2-carboxylate and Cyanoacetamide: Formation of 3-Keto-4-cyano-1-hydroxy-2:3:5:6:7:8-hexahydroisoquinoline* (VI).—The ethyl *cyclo*hexanone-2-carboxylate was prepared from *cyclo*hexanone and ethyl oxalate according to Kötz and Michael's method (*Annalen*, 1906, **350**, 210) and obtained as a colourless liquid, b.p. 104-107°/10 mm. The yield was about 65 per cent. of the weight of *cyclo*hexanone used. The condensation was effected both by

Knoevenagel's as well as by Michael's reaction. The former was conducted under the usual conditions and the latter as follows. To an alcoholic suspension of sodiocyanoacetamide prepared from an alcoholic solution of cyanoacetamide (8·4 g.) and sodium (2·3 g.) dissolved in absolute alcohol, an alcoholic solution of ethyl *cyclo*hexanone-2 carboxylate (17·0 g.) was gradually added with shaking. Soon the sodium salt dissolved and within a few minutes the contents of the flask changed into a thick sludge. It was left overnight. After 24 hours water was added and acidifying the clear solution a crystalline precipitate was obtained. The yield was about 85 per cent. On crystallisation from water or acetic acid it melted at 278° (decomp). (Found : N, 14·89,14·92. $C_{10}H_{10}O_2N_2$ requires N, 14·74 per cent.). The compound is soluble in boiling alcohol, alkali and in alkaline carbonate with effervescence. It imparts a deep bluish-violet coloration to alcoholic ferric chloride, but gives no colour reaction with sodium nitrite solution. On adding a concentrated solution of caustic potash, a potassium salt of the compound separated out. This crystallises from boiling water in small needles. (Found: K, 15·81. $C_{10}H_9O_2N_2K,H_2O$ requires K, 15·85 per cent.).

Hydrolysis: *Formation of* 1:3-*Dihydroxy*-5:6:7:8-*tetrahydro*-iso*quinoline*.—The cyanoisoquinoline derivative (2 g.) was heated with fuming hydrochloric acid (20 c.c.) at 180° for about 5 hours. The reacted mixture on partial neutralisation with sodium carbonate gave a product which on crystallisation from alcohol (charcoal) melted at 205°. (Found: N, 8·65. $C_9H_{11}O_2N$ requires N, 8·48 per cent.). It is soluble in boiling water and in most organic solvents. It gives with sodium nitrite a bluish-green coloration on boiling. Ferric chloride gives a red coloration but it soon vanishes away. The dihydroxy compound dissolves in alkali and sodium carbonate solution with effervescence and forms a hydrochloride with concentrated hydrochloric acid, too soluble in water. It also reduces an ammoniacal solution of silver nitrate on boiling.

Methyl Derivative:3-*Keto*-4-*cyano*-1-*hydroxy*-2-*methyl*-2:3:5:6:7:8-*hexahydro*isoquinoline (VI, NH=NMe).—Ethyl *cyclo*hexanone-2-carboxylate was treated with sodiocyanoacetmethylamide in the same way as in the previous case. After 8 days the reacted mixture was concentrated on the water-bath and acidified with hydrochloric acid. The solid which separated, on crystallisation from boiling water was obtained in small prismatic needles with a mole-

cule of water of crystallisation, m.p. 199°. (Found: N, 12·52; H_2O, 7·84. $C_{11}H_{12}O_2N_2$, H_2O requires N, 12·61; H_2O, 8·10 per cent.). The anhydrous *iso*-quinoline derivative obtained by heating the substance in an air-bath at 110° melted at 202-203°. (Found: N, 13·56. $C_{11}H_{12}O_2N_2$ requires N, 13·73 per cent.). The compound is easily soluble in alcohol, difficultly in chloroform and ether and almost insoluble in benzene. It dissolves in sodium carbonate solution with effervescence, forms a silver salt, reduces a hot ammoniacal solution of silver nitrate and with ferric chloride solution gives a green coloration but it is very fugitive.

Ethyl Tetrahydroanthranilate and Cyanoacetamide.—The anthranilate derivative (VIII) was prepared by passing ammonia to ethyl *cyclo*hexanone-2-carboxylate (Dieckmann, *Annalen*, 1901, 317, 27) and was heated with a molecular quantity of cyanoacetamide in an oil-bath at 120° for about 25 minutes. The solid found on crystallisation from dilute alcohol containing a trace of ammonia was obtained in clusters of needles, m.p. 320° with decomposition sintering and moistering earlier. (Found: N, 20·32. $C_{10}H_9O_2N_2 \cdot NH_4$ requires N, 20·29 per cent.) This is the ammonium salt of 3-keto-4-cyano-1-hydroxy-2:3:5:6:7:8-hexahydro*iso*quinoline. It is easily soluble in water and when its aqueous solution is treated with hydrochloric acid, the free compound, was isolated and melted at 278° with decomposition, not depressed when admixed with the *iso*quinoline derivative obtained from ethyl *cyclo*hexanone-2-carboxylate. The compound itself or its hydrolysis product gradually becomes coloured.

The tetrahydroanthranilate when heated with benzalbenzoylacetone in alcoholic solution at 50° for about 5 days afforded no condensation product. On the contrary, smell of benzaldehyde and and ethyl *cyclo*hexanonecarboxylate was distinctly perceived and the reaction mixture was completely soluble in ether (*cf.* Knoevenagel, *loc. cit.*).

Ethyl 5-Methyl-cyclohexanone-2-carboxylate and Cyanoacetamide: Formation of 3-Keto-4-cyano-6-methyl-1-hydroxy-2:3:5:6:7:8-hexahydroisoquinoline (XIV).—The β-ketonic ester was prepared from *m*-methyl*cyclo*hexanone which yields more than 60% of its weight of ethyl 5 methyl*cyclo*hexanone-2-carboxylate as a colourless oil boiling at 137-140°/25 mm. The condensation was effected with sodiocyanoacetamide in the usual way. The yield is almost theoretical. The compound crystallises from dilute alcohol in small

rectangular prisms, m.p. 271-72° (decomp). It slowly takes a pink tinge by coming in contact with air. (Found: N, 13·51. $C_{11}H_{12}O_2N_2$ requires N, 13·73 per cent.). It is soluble in sodium carbonate solution, gives with ferric chloride a deep bluish-violet coloration but no coloration with sodium nitrite.

Hydrolysis: Formation of 6-Methyl 1:3-dihydroxy-5:6:7:8-tetrahydroisoquinoline (XV).—The above compound on heating with hydrochloric acid in the usual way afforded a solid which after crystallisation from dilute alcohol melted at 200°. (Found: N, 8·15. $C_{10}H_{13}O_2N$ requires N, 7·82 per cent.). With sodium nitrite solution it gives no sharp coloration and with ferric chloride gives a light pink colour which soon disappears, but is easily soluble in alkali and alkaline carbonate solutions.

Benzoylacetoneamine and Cyanoacetamide: Formation of 3-Cyano-4-methyl-6-phenyl-2-pyridone.—Benzoylacetoneamine (Knoevenagel, *Ber.* 1903, **36**, 2187) and cyanoacetamide in molecular proportions when heated at 150° for about half an hour gave rise to a crystalline product with evolution of ammonia. This crystallises from glacial acetic acid in shining plates with a faint violet reflex, m.p. 310°. (Found: N, 13·35. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.). It was found to melt at the same temperature when mixed with with an authentic sample of 3-cyano-4-methyl-6-phenyl-2-pyridone (Basu, *loc. cit.*). Treating its sodium salt with methyl iodide in methyl alcoholic solution 3-cyano-1:4-dimethyl-6-phenyl-2-pyridone was obtained. This crystallises from alcohol in long prismatic needles with a violet reflex, m.p. 265° (*cf.* Bardhan, *J. Chem. Soc.*, 1929, p. 2228). (Found: N, 12·63. $C_{14}H_{12}ON_2$ requires N, 12·5 per cent.). The compound is insoluble in caustic alkali. On hydrolysis with hydrochloric acid in the usual way an oil was isolated on neutralising the acid solution. The oil was extracted with ether. The ethereal solution was dried and dry hydrogen chloride was passed into it when crystal began to separate and this on recrystallisation from dilute hydrochloric acid melted at 163°, sintering earlier. (Found: N, 6·19; Cl, 14·87. $C_{13}H_{13}ON$, HCl requires N, 5·94; Cl, 15·07 per cent.). The compound when heated to its melting point gave hydrochloric acid fumes. The hydrochloride or the free base itself does not give any sharp coloration with alcoholic ferric chloride.

Methylacetylacetoneamine and Cyanoacetamide: Formation of 3-Cyano-4:5:6-trimethyl-2-pyridone.—Methylacetylacetoneamine was

prepared by shaking with liquor ammonia (*cf.* Combes and Combes, *Bull. Soc. Chim.*, 1893, *iii*, 7, 778) and crystallised from a mixture of chloroform and petroleum ether, m.p. 112°. (Found: N, 12·53. $C_6H_{11}ON$ requires N, 12·39 per cent.). Its alcoholic solution with ferric chloride gives no appreciable colour. The condensation with cyanoacetamide was brought about in the usual way. The crystals obtained, melted at 306° after crystallisation from alcohol and was found to be identical with the compound 3-cyano-4:5:6-trimethyl-2-pyridone previously obtained from methylacetylacetone and cyanoacetamide in presence of piperidine (Basu, *loc. cit.*). But when the amine was heated with benzalbenzoylacetone in an oil-bath at 120-25° for about 8 hours no definite condensation product was isolated.

Benzalbenzoylacetone and p-*Toluoylacetoneamine*: *Formation of* 2-*Methyl*-4: 6-*diphenyl*-3-p-*toluoyl*-5-*acetyl*-1: 4-*dihydropyridine* (XIII).—Benzalbenzoylacetone was prepared according to Knoevenagel and Erler (*Ber.*, 1903, **36**, 2131) and obtained in shining crystals, m.p. 99°, from petroleum ether. This (3 g.) was heated with *p*-toluoylacetoneamine (2·1 g.) on an oil-bath at 120° for 5 hours. The reaction mixture was treated with a few c.c. of alcohol when a yellow crystalline product (about 2·2 g.) separated out. This on crystallisation from alcohol (charcoal) melted at 183°. (Found: C, 82·09; H, 6·55; N, 3·31. $C_{28}H_{25}O_2N$ requires C, 82·55; H, 6·14; N, 3·44 per cent.). It is easily soluble in warm chloroform, benzene and acetic acid but insoluble in petroleum ether. It dissolves in concentrated sulphuric acid with an intense red coloration but is precipitated unchanged on dilution with water.

In conclusion, the author wishes to express his sincere thanks to Professor H. K. Sen, for placing the resources of his laboratory at the author's disposal.

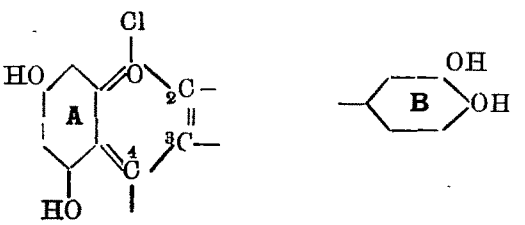
Department of Applied Chemistry,
University College of Science and Technology,
Calcutta.

Received March 19, 1931.

On the Constitution of Cyanidin Chloride.*

By M. Nierenstein.

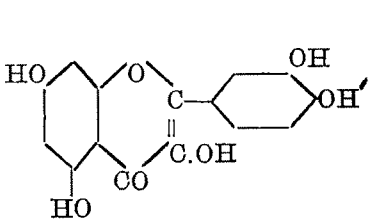
The classical researches of Willstätter have established beyond doubt the presence of the 5:7-dihydroxypyrylium-ring in the anthocyanidins, the red and blue pigments of a large number of flowers. In this ring the positions 2, 3 and 4 are substituted by H, OH and a hydroxylated benzene nucleus. Thus cyanidin, the colouring matter of the corn-flower, the rose and the poppy, which Willstätter has shown to give a beautifully crystallising chloride, $C_{15}H_{11}O_6Cl$, yields phloroglucinol and protocatechuic acid on hydrolysis.



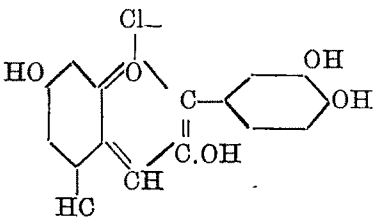
As will be realised, any of the *six* possible formulae of cyanidin would yield phloroglucinol and protocatechuic acid, derived from the nucleus **A** and **B** respectively on hydrolysis, and until more is known as to the fate of the three carbon atoms 2, 3 and 4 during hydrolysis any formula suggested for cyanidin is of a highly speculative character. In spite of this, Formula (II) was assigned by Willstätter to cyanidin (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 769) since quercetin (I) is supposed to yield cyanidin chloride (II) on reduction

* From a paper entitled "Rise and Fall of a Biochemical Hypothesis", communicated to the Indian Science Congress at Nagpur, January, 1931.

in hydrochloric acid solution, magnesium, zinc dust or sodium amalgam being used as a reducing agent.



(I)



(II)

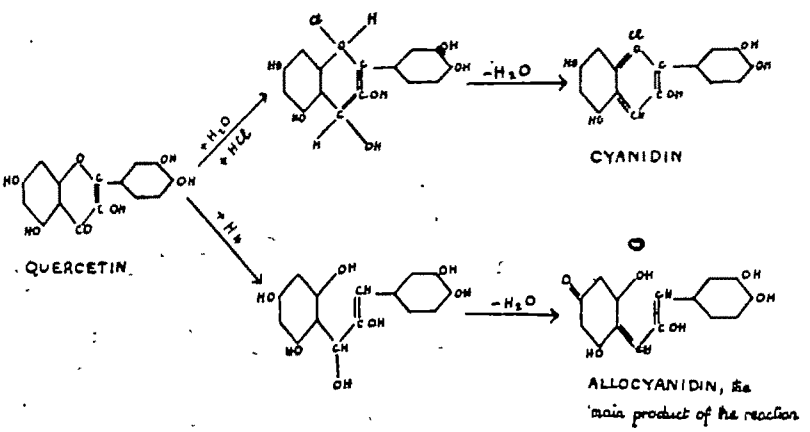
The supposed reduction of an anthoxanthone (quercetin) to an anthocyanidin (cyanidin) is of particular interest not only to chemists but also to botanists, as it offers a chemical explanation of the inter-relationship between these two groups of plant pigments so well known to all who follow the colour changes in plants, where starting from a very insignificant yellow coloured stock some of the most beautiful reds, pinks and blues have been produced. Stein (*J. pr. Chem.*, 1862, **85**, 351; 1863, **88**, 280; 1863, **89**, 4491), already noticed that yellow plant extracts turn deep red on reduction with zinc dust and hydrochloric acid. His observations were confirmed by Hlasiwetz and Pfaundler (*Sitzungsber. Wiener. Akad.*, 1864, **50**, 6), who further observed that these red coloured solutions turn blue-green on the addition of alkali, *the* specific reaction of the anthocyanidins already known to Robert Boyle and fully described by him in 1664 in his "Experiments and Considerations touching Colour." It was therefore not surprising that Hlasiwetz and Pfaundler should have claimed to have reduced the anthoxanthones to the anthocyanidins.

The reduction theory has since been generally favoured by chemists. It is, however, noteworthy that botanists were strongly of the opinion that if there is any inter-relationship between the anthoxanthones and the anthocyanidins, it was due to oxidation and not to reduction (compare, for example, Gertz, "Studier öfver Anthocyan", Lund, 1906; Onslow, "The Anthocyanin Pigments of Plants," Cambridge, 1925). It will be realised that botanical evidence was thus contrary to the chemical interpretation put forward by the supporters of the reduction theory which has in recent years been upheld particularly by Everest and Willstätter.

Everest (*Proc. Roy. Soc.*, 1914, B, **87**, 444), in a series of qualitative experiments which were identical with those described by Hlasiwetz and Pfaundler, claimed to have synthesised several anthocyanidins,

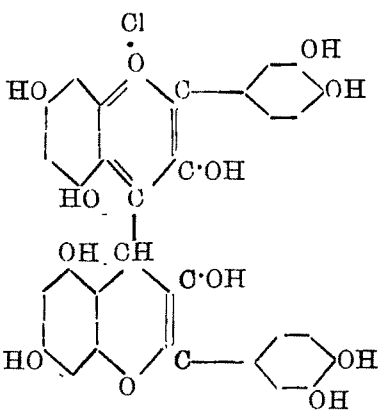
although in no case were the products analysed or even isolated. Encouraged by these qualitative experiments, Everest put forward a general scheme for the reduction of the anthocyanidins as illustrated in the reduction of quercetin to cyanidin chloride.

Willstätter and Mallison (*Sitzungsber. Preuss. Akad. Wiss.*, 1914, 769), who had previously (*ibid*, p. 402) expressed themselves against the view that the anthoxanthones may be reduced to anthocyanidins, soon after the publication of Everest's paper announced the *synthesis* ofthe cyanidin, which they claimed to have obtained on reduction of quercetin. They pointed out, however, that Everest's product was not true cyanidin, but a substance to which they assigned the name *allo*cyanidin, and that true cyanidin is only formed in minute quantities from quercetin. The true cyanidin, which they obtained in a crystalline form and which they subjected to analysis, they found to be in every respect identical with natural cyanidin from corn-flowers and roses. The mechanism of the reaction leading to the production of cyanidin and *allo*cyanidin was shown by Willstätter and Mallison as follows:—

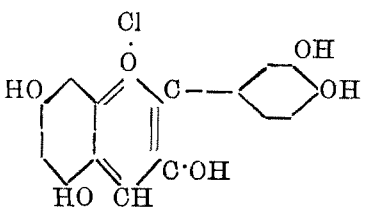


The chemistry underlying the production of Willstätter's *allo*cyanidin was queried by Pummerer ("Organische Chemie," 1921, p. 127), which is not surprising considering the abnormality of its supposed formation. In a similar way it was pointed out by Malkin and

Nierenstein (*J. Amer. Chem. Soc.*, 1930, **52**, 2864) that the production of cyanidin chloride from quercetin is quite unexpected since fluorone, xanthone, thioxanthone, acridone, anthraquinone, pyrone and their derivatives lead to *dimolecular* products on reduction in acid solution. Since quercetin is a pyrone-derivative it was hard to see why it should not conform to this general rule established by Baeyer and Piccard (*Annalen*, 1911, **384**, 208; 1915, **407**, 346). Malkin and Nierenstein therefore reinvestigated this reduction process and they were able to show that the reaction proceeds *normally* leading to the production of quercetylene chloride (III) and not to 3:5:7:3′:4′-pentahydroxyflavylium chloride (IV, cyanidin chloride).



(III)



(IV)

The following quotation from the memoir by Malkin and Nierenstein explains the reason why Willstätter and Mallison were misled in believing that they reduced quercetin to cyanidin chloride:

"The remarkable similarity between quercetylene chloride, $C_{30}H_{21}O_{12}Cl+2H_2O$. and cyanidin chloride, $C_{15}H_{11}O_6Cl$, which not only resemble each other in almost all respects, but require exactly the same carbon content (C, 55·8), easily accounts for the fact that Willstätter and Mallison should have assumed that they had synthesised cyanidin chloride, since owing to the scarcity of material (0·165 g.) at their disposal, no chlorine analysis, which would have clearly emphasised the difference between these two substances, was possible."

However, not only quercetylene chloride (III) but also 3:5:7:3′:4′-pentahydroxyflavylium chloride (IV) has been shown by Willstätter, Zechmeister and Kindler (*Ber.*, 1924, **57**, 1944) and by Pratt and Robinson (*J. Chem. Soc.*, 1925, **127**, 172, 1180) to be in every respect identical with natural cyanidin chloride. The position therefore is: two *different* substances A (quercetylene chloride) and B (3:5:7:3′:4′-pentahydroxyflavylium chloride) have been proved to be in every respect identical with C (natural cyanidin chloride), which is perturbing.

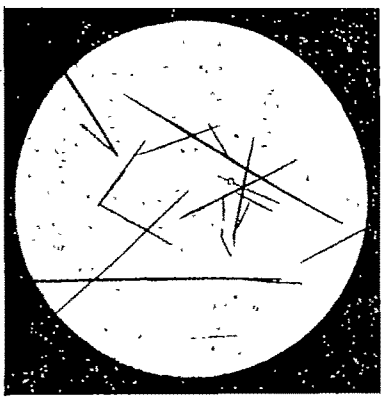
The comparisons between the natural and synthetic products are based (1) on a series of colour reactions, (2) on the absorption spectra and (3) on the general crystallographical appearance of the substances in question, as unfortunately neither the natural nor the synthetic products possess melting points. Such methods do not yield orthodox evidence of identity and are scarcely convincing.

(1) *Colour Reactions.*—Purely *qualitative* colour reactions were originally used in the comparisons between the natural and synthetic products. The application of *quantitative* methods as elaborated by Malkin and Nierenstein (*Ber.*, 1928, **61**, 796) and by Fear and Nierenstein (*Biochem. J.*, 1928, **22**, 615) revealed some striking differences between natural cyanidin chloride and the synthetic product. Thus, for example, cyanidin chloride turns pure blue at p_H 8·04 with alkali, whereas 3:5:7:3′:4′-pentahydroxyflavylium chloride (synthetic cyanidin chloride) requires as high a p_H as 11·57 to give pure blue. However, in any case nothing can be deduced from the colour reactions as to the constitution of flavylium salts, as pointed out by Buck and Heilbron (*J. Chem. Soc.*, 1923, **123**, 2524) who showed that substitution in positions 2 and 4 in the pyrylium-ring leads to compounds which are remarkably similar in their colour reactions.

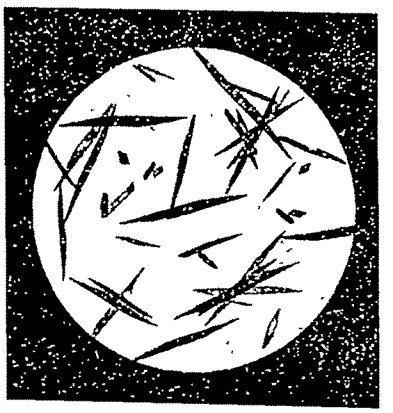
(2) *Absorption Spectra.*—The absorption spectra of the anthocyanidins have been studied by a large number of investigators, and special reference must be made to the very valuable contribution by Schou (*Helv. Chim Acta*, 1927, **10**, 910) who has shown that two such different substances as peonidin chloride and malvidin chloride give the same absorption spectra.

(3) *Crystallographical Appearance.*—Here special attention must be drawn to a paper by Kuhn and Wagner-Jauregg (*Ber.*, 1928, **61**, 2506) who find that natural cyanidin chloride and the synthetic product, if crystallised under *identical* conditions, lead to crystal forms

which differ fundamentally as illustrated in the accompanying photographs.



Cyanidin chloride.



3 :5 :7 :3′ :4′-Pentahydroxy-flavylium chloride.

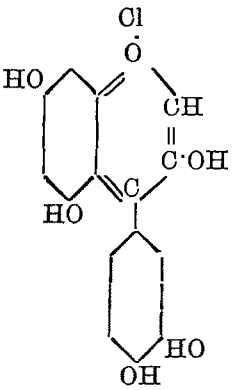
Far more convincing is the fact established by Willstätter and Everest (*Annalen*, 1913, **401**, 231,) that natural cyanidin chloride yields a definite, well-crystallising product on oxidation, whereas it was shown by Pratt and Robinson (*J. Chem. Soc.*, 1925, **127**, 172) that no such oxidation product can be obtained from synthetic 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride. Malkin and Nierenstein have confirmed the observations of Willstätter and Everest and of Pratt and Robinson with the natural and synthetic products respectively. This in itself suffices to establish the fact that cyanidin chloride is *not* 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride. They also showed that the oxidation product from natural cyanidin chloride is not quercetin, as believed by Combes (*Compt. rend.*, 1913, **157**, 1002, 1454) who assumed that quercetin and cyanidin are interconvertible in the living plant.

In conclusion, attention may also be drawn to the following:—

(1) That X-ray analyses of cyanidin chloride and 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride (synthetic cyanidin chloride) show *not a single* crystal spacing which is common to both substances, as already published by Malkin and Nierenstein (*Ber.*, 1928, **61**, 794).

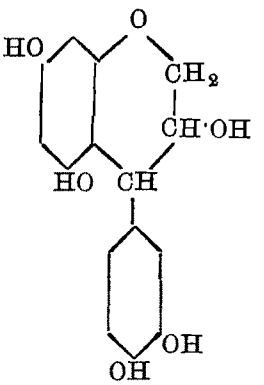
(2) That Freudenberg (*Annalen*, 1925, **444**, 143) has succeeded in reducing cyanidin chloride to epi-catechin. From a series of investigations published by the author it is evident that catechin is

represented by formula (VI), which would suggest formula (V) for cyanidin chloride.



(V)

Cyanidin chloride [?]



(VI)

Catechin

It is not, however, suggested with any degree of certainty that cyanidin chloride is represented by this formula, since up till now neither the epimerisation of catechin to Freudenberg's epicatechin (Nierenstein, *J. Indian Chem. Soc.*, 1930, 7, 279) nor its production from cyanidin chloride on reduction has been confirmed.

THE UNIVERSITY, BRISTOL, ENGLAND.

Received January 8, 1931.

Studies in the Coagulation of Colloids from the Standpoint of Smoluchowski's Theory. Part II. Coagulation of Arsenious Sulphide Sol.

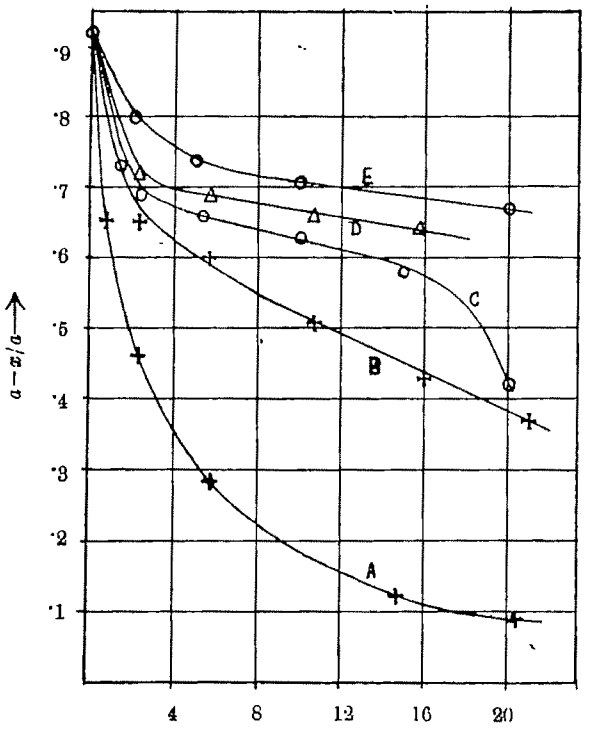
By Shridhar Sarvottam Joshi and S. Madhava Prabhu.

The coagulation of the arsenious sulphide sol during its transition from the *rapid* to the *slow* region has been examined employing the method used in Part I (*J. Indian Chem. Soc.*, 1931, **8**, 11).

Experimental.

The same method of preparing the colloid was followed with the difference that the excess of hydrogen sulphide was removed by a current of hydrogen. A convenient amount of the sol (0·92 g. As_2S_3 per litre in all experiments), and of the coagulator solution were kept in a thermostat (15°); 10 c.c. from each of the solutions were introduced simultaneously at a known time in a reaction vessel kept in the thermostat. The coagulating sol was then filtered at different intervals. a, the initial colloid-content of the sol, $a-x$, that of the filtrate at a given time t, were estimated volumetrically by Kessler's method (*Pogg. Ann.*, 1863, **118**, 17). Standard ferrous sulphate solution was used and the colloid-contents are expressed as g. of As_2S_3 per litre. The times taken for mixing the colloid and the coagulator solution, and for subsequent filtration were noted, and though small, are included in the time t. Curves A, B, C, D, E, in Fig. 1 show the progress of coagulation due to different electrolyte concentrations. β, the Smoluchowski's constant, calculated from, $\beta=\frac{1}{t}\left[\sqrt{\frac{n_0}{n_t}}-1\right]$...(1), and k, the bimolecular constant were calculated as previously (Part I, *loc. cit.*) from values in Tables 1—5, which were obtained from the corresponding curves of Fig. 1. The calculation of results in Tables VI, VII is explained later.

FIG. 1.



A, 0·1370 N-H_2SO_4 in mixture.
B, 0·1265 N- ,, ,, ,,
C, 0·1174 N- ,, ,, ,,
D, 0·1028 N- ,, ,, ,,
E, 0·0912 N- ,, ,, ,,

TABLE I.

0·1370 *N*-H_2SO_4. (Fig. 1. Curve A.)

Time (min.) ...	1	2	4	6	8	10	14	16
$a-x$ ...	0·70	0·51	0·36	0·27	0·22	0·18	0·14	0·12
β ...	0·15	0·17	0·15	0·14	0·18	0·126	0·11	0·10
x ...	0·30	0·49	0·64	0·73	0·78	0·82	0·86	0·88
k ...	0·31	0·40	0·39	0·40	0·40	0·41	0·40	0·42

TABLE II.

0·1265 *N*-H_2SO_4. (Fig. 1. Curve B.)

Time (min.) ...	1	2	4	8	11	14	16	18
$a-x$ ...	0·75	0·68	0·61	0·54	0·50	0·45	0·43	0·41
β ...	0·11	0·082	0·056	0·038	0·032	0·030	0·029	0·029
x ...	0·25	0·32	0·39	0·46	0·50	0·55	0·57	0·59
k ...	0·23	0·18	0·13	0·088	0·076	0·075	0·071	0·069

TABLE III.

0·1174 N-H_2SO_4. (Fig. 1. Curve C.)

Time (min.) ...	1	2	4	6	10	12	14	16	18
$a-x$ ...	0·77	0·71	0·67	0·65	0·63	0·615	0·595	0·555	0·505
β ...	0·11	0·069	0·043	0·031	0·021	0·019	0·019	0·018	0·019
x ...	0·23	0·29	0·33	0·35	0·37	0·385	0·405	0·445	0·495
k ..	0·20	0·15	0·093	0·069	0·046	0·041	0·039	0·041	0·045

TABLE IV.

0·1028 N-H_2SO_4. (Fig. 1. Curve D.)

Time (min.) ...	1	2	5	10	15
$a-x$ ...	0·84	0·75	0·69	0·67	0·645
β ...	0·046	0·05	0·031	0·017	0·013
x ...	0·16	0·25	0·31	0·33	0·355
k ...	0·19	0·17	0·09	0·049	0·037

TABLE V.

0·0912 N-H_2SO_4. (Fig 1. Curve E.)

Time (min.) ...	2	5	10	20
$a-x$ ...	0·80	0·74	0·71	0·67
β ...	0·036	0·023	0·014	0·0086
x ...	0·20	0·26	0·29	0·33
k ...	0·13	0·07	0·041	0·025

TABLE VI.

T for $a-x=0·69$ Curve A, taken as unity.

Coagulator.	Time (min.).	T_n/T.	C/C_n.	P.
A	1·15	1·0	—	—
B	1·7	1·48	1·082	5·0
C	2·75	2·39	1·167	5·6
D	5·0	4·35	1·382	5·1
E	15·0	13·1	1·502	6·8

TABLE VII.

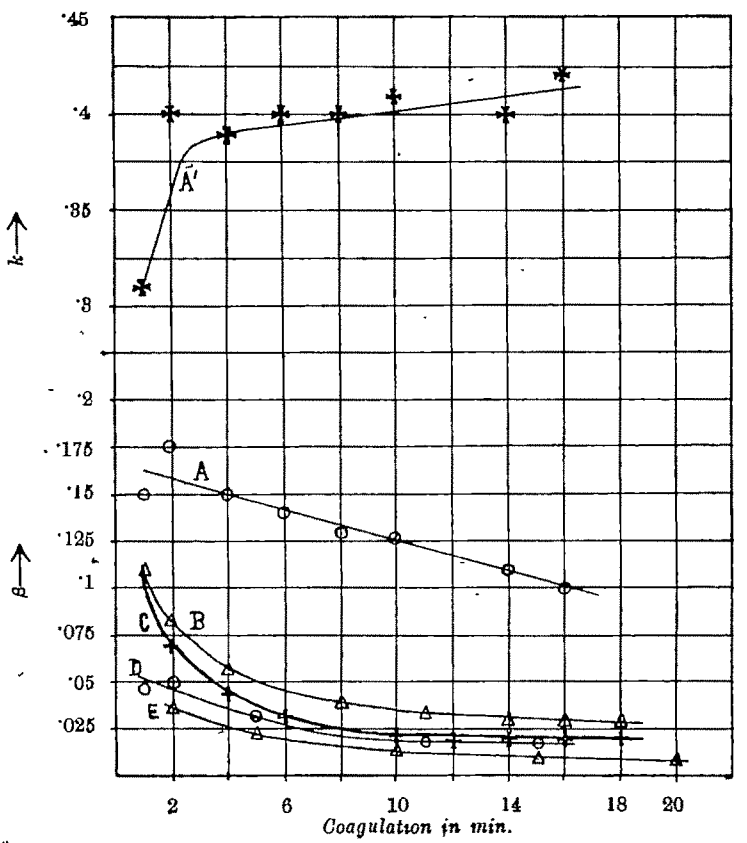
T for $a-x=0{\cdot}67$, Curve B, taken as unity.

Coagulator.	Time (min.).	T_x/T.	C/C_x.	P.
A	1·2	0·52	0·924	8·2
B	2·3	1·0	1·0	—
C	4·0	1·74	1·08	7·4
D	9·3	4·04	1·23	6·7
E	20·0	8·7	1·39	6·6

Discussion.

From these results it is seen that for the maximum concentration of the electrolyte (Table I; Curve A, Fig. 1), β, the Smoluchowski's constant decreases on an average by about 7% during the first 8 minutes, in which about 74% of the sol is coagulated. This shows that the coagulation is very near the *rapid* region. Furthermore, the β—time curve in the above case (curve A, Fig. 2) lies apart from other curves corresponding to lower electrolyte concentrations (B—E, Fig. 2).

FIG. 2.



That this coagulation is almost *rapid* is also indicated by the tendency of k, the bimolecular constant to increase especially during the early stage (Table I; Curve A′, Fig. 2), since the deduction from Smoluchowski's theory (*Z. Phys. Chem.*, 1917, **92**, 129), *viz.*, that k should increase with time during both slow and rapid coagulations, holds in general only in the latter. The other series (Tables II—V) show a diminution of β with time, which is characteristic of slow coagulation. In these series, β decreases appreciably soon after the start of coagulation (Curves B—E, Fig. 2), which shows that the deviation from Smoluchowski's theory occurs mainly during the early stages. This is contrary to the observations of Mukherjee and Majumdar (*J. Chem. Soc.*, 1924, **125**, 785) on the slow coagulation of arsenious sulphide sol. Using the equation,

$$\Sigma n = n_0/1+\beta t \qquad \ldots \quad (2)$$

and assuming that Σn, the total number of particles is measured by the corresponding relative transparency, they found that the relative times (which are proportional to $1/\beta$) for a given value of Σn during different coagulations varied markedly after the initial stages of coagulation. Desai (*Trans. Faraday Soc.*, 1928, **24**, 191) has made similar observation in the slow coagulation of the tungstic acid sol, studied by a method similar to that employed by Mukherjee and Majumdar. Anderson's results on the slow coagulation of the gold sol, however, show just the opposite (*Trans. Faraday Soc.*, 1924, **19**, 628). He estimated the number of primaries at the time t by a colorimetric method due to Hatschek (*ibid.*), and calculated β from equation (2). It is seen from his results that the diminution of β resembles the present observations. It is suggested that this divergence of results regarding the variation of β during coagulation might in part be ascribed to the approximation involved in estimating Σn and n_t which occur in equations (1) and (2) respectively. It may be pointed out that with the exception perhaps of the ultramicroscopic method, the continuous variability during coagulation, is practically the only criterion we have for adopting any given property as a measure of coagulation, especially in the case of polydisperse sols, (that is, in respect of Σn and n_t).

It is seen from the results in Tables I—V, that contrary to the requirements of Smoluchowski's theory, the bimolecular constant, k diminishes during coagulation. Similar results were obtained by

Anderson (*loc. cit.*) and by the authors in the slow coagulation of the antimony sulphide sol, using the present method of measuring coagulation (Part I, *loc. cit.*). On plotting k against coagulation time, regular curves were obtained, closely resembling the corresponding β—time curves in Fig. 2.

It is seen from Fig. 1 that the coagulation—time curves are not markedly *affine*, as would be the case if *slow* coagulation differed from *rapid*, only by a constant multiple of the velocity constant for the latter (Smoluchowski, *loc. cit.*). A number of workers (*cf.* Desai, *loc. cit.*) also Freundlich (*Colloid and Capillary Chemistry*, 1926, pp. 434-447) regard slow coagulation as essentially autocatalytic, and not amenable to a simple extension of Smoluchowski's equation deduced for rapid coagulation. The chief support for this view is derived from the fact that in a number of cases, (*i*) the coagulation—time curve has an **S**-shape, indicating acceleration of an initial slow change, and that, (*ii*) the following equation characteristic of an autocatalytic reaction holds:—

$$\frac{dx}{dt}=k_1\,(1-bx)\,(1-x) \qquad \ldots \quad (3)$$

where k_1 and b are constants; b is evaluable from the inflection on the x—time curve, and is practically independent of the coagulator concentration. k_1 corresponds to β. It will be seen from the results in Fig. 1 that the nature of the $(a-x)$—time curves does not support (*ii*). k_1 in (*i*) was not constant in any of the series in Fig. 1, *e.g.* in the coagulation corresponding to the curve C, k_1 varied from 0·007 to 0·0058. In this connection it may be pointed out that Freundlich (*loc. cit.*), and Freundlich and Basu (*Z. Phys. Chem.*, 1925, **115**, 208) obtained evidence to show that in a number of coagulations, the observed autocatalysis was ascribable to secondary factors, such as part of the coagulum serving as coagulation nuclei, the removal of which by stirring eliminated the effect. Mukherjee and Majumdar (*loc. cit.*) found however without observing the special precautions as to stirring, etc., that a number of slow coagulations of colloidal arsenious sulphide sol did not show any sign of autocatalysis. It would appear, therefore, that whilst some changes might be subject to this effect, it can not be considered as a general characteristic of slow coagulation.

Such a characteristic is obtained in the very marked influence of the electrolyte concentration on the rate of slow coagulation. According to Paine (*Koll.-Chem. Beih.*, 1912, **16**, 430), we have

$$\frac{T_n}{T}=\left(\frac{C}{C_n}\right)^P \text{, or } P=\frac{\log T_n-\log T}{\log C-\log C_n} \quad \ldots (4)$$

where T and T_n denote times for attaining the same stage of coagulation at electrolyte concentrations C and C_n respectively. The results of applying this equation to two series (curves A and B, Fig. 1) are given in Tables V and VI. It is seen that P varies from 5 to 8. The results of Paine (*loc. cit.*), Gann (*Koll.-Chem. Beih.*, 1916, **8**, 63), Desai (*loc. cit.*), and of Hatschek (*Trans. Faraday Soc.*, 1921, **17**, 499) show that the value of P depends upon the nature of the coagulating sol, and is approximately constant over a limited range of coagulator concentrations. We found that P varied considerably with the concentration of the coagulator taken as standard (also, *cf.* Desai, *loc. cit.*). For instance with $\frac{a-x}{a}=\cdot 6$, and taking the electrolyte concentration corresponding to curve C (Fig. 1) as standard, P was found to be as high as 16. It is to be anticipated therefore that the lower the coagulator concentration, C, the greater is the influence of a given increase in C, in increasing the rate of coagulation. This agrees with the change from almost nil coagulation to one of a low but finite rate, due to but a slight increase in the strength of the coagulator solution in the region of the so-called *threshold* concentration, which indicates a comparatively high value for P, and with the fact that in the *rapid* region, the rate of coagulation, which is measured by $\frac{1}{T}$ in (4), is independent of C. It follows therefore, that for large values of the last quantity P must tend to zero as a limit.

THE CHEMICAL LABORATORIES,
BENARES HINDU UNIVERSITY,
BENARES.

Received March 5, 1931.

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XII. The Rotatory Dispersion of Stereoisomeric Anilino-, Toluidino- and Naphthylamino-methylenecamphors.

By Bawa Kartar Singh, Bhutnath Bhaduri and Taraprosad Barat.

In this communication we present new experimental data on the rotatory dispersion of the condensation products of oxymethylenecamphors (*d*, *l* and *dl*) with aromatic *mono*amines, namely, aniline, *m*- and *p*-toluidines, α- and β-naphthylamines.

α-Naphthylaminomethylenecamphors (*d*, *l* and *dl*) exist in two dimorphous forms. The higher melting form, in each case, is obtained direct by the condensation of the corresponding oxymethylenecamphor with α-naphthylamine. It is converted into the lower melting form by crystallisation from methyl alcohol with *prolonged digestion*. The rotatory dispersions of the two forms of the *dextro*- and *laevo*-enantiomers are identical (Tables XIX-XXX) which characterise them as dimorphous (Singh, *J. Indian Chem. Soc.*, 1929, **6**, 1007).

p-Toluidinomethylene-*d*-camphor melts at a lower temperature than that recorded by Bishop, Claisen and Sinclair (*Annalen*, 1894, **281**, 359), but it has the same rotatory power as that recorded by Pope and Read (*J. Chem. Soc.*, 1909, **95**, 171). It appears that our lower melting form is a dimorphous modification of the one prepared by Claisen and his co-workers, but we have not been able to convert it into the higher melting form. Similarly anilinomethylene-*d*-camphor prepared by us melts at a lower temperature than that of Claisen and co-workers (*loc. cit.*). A similar explanation for the discrepancy based on polymorphism may be advanced, though in this case also we have not succeeded in obtaining the higher melting forms. The condensation products of *o*-toluidine with the oxymethylenecamphors are oils, which refused to crystallise.

The Influence of Chemical Constitution on the Character of Rotatory Dispersion.—Biot classified rotatory dispersions into two

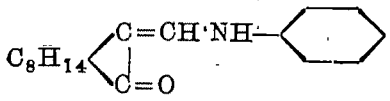
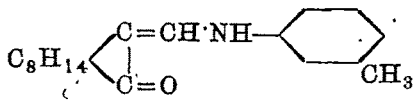
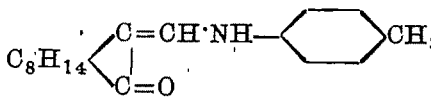
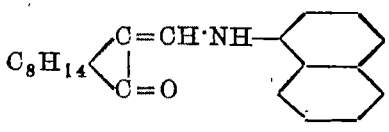
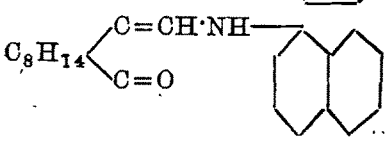
groups, as they did, or did not, obey the laws of inverse squares. Recent work has shown that this law is generally not obeyed exactly, although some substances, such as sodium tartrate (Lowry and Austin, *Phil. Trans.*, 1922, [A], 222, 249) and the *dextro-* and *laevo-*forms of *p*-iodophenylacetylaminocamphor (Singh, Mallick, and Bhaduri, *J. Indian Chem. Soc.*, 1931, 8, 95) obey it very nearly. Rotatory dispersions are however classified as "*simple*" or "*complex*", according as they can, or cannot, be expressed by the equation, $[\alpha]=\frac{k}{\lambda^2-\lambda^2_0}$. Oxymethylenecamphors and their condensation products with aromatic diamines (Singh and Bhaduri, *J. Indian Chem. Soc.*, 1930, 7, 771; 1931, 8, 181) were found to obey the simple dispersion formula exactly. These compounds which contain 2 or 4 asymmetric carbon atoms respectively are complex ring compounds loaded with double bonds. It is now found that the rotatory dispersions of the *aryl* derivatives of aminomethylenecamphors now described, can also be expressed exactly by the one term equation of Drude. The nature of the solvent is found not to produce any change in the type of rotatory dispersion in this series, as is seen from the extensive measurements recorded in Tables I—XXXVI.

The value of λ_0, the hypothetical absorption band in the ultra-violet, deduced from the dispersion equation, varies with the nature of the solvent, except for *p*-toluidinomethylenecamphor, the rotatory dispersion of which is expressed by the same equation in chloroform and pyridine (Tables XVI and XVIII). Its variation is of the same order as that of the rotatory power of the compound and the dielectric constant of the solvent in two cases, namely, anilino- and *p*-toluidinomethylenecamphor. In the remaining cases no such simple relationship can be traced, except that its value is lowest in benzene which has the lowest dielectric constant and gives the lowest rotatory power (Table A).

The Influence of Solvent on the Rotatory Power.—The specific rotatory power for mercury green line of the five compounds in different solvents are given in Table A. It is found that the order of decreasing rotatory power is methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene, except for α-naphthylaminomethylenecamphor in pyridine and chloroform and *m*-toluidinomethylenecamphor in acetone and ethyl alcohol in which cases the order is reversed (*cf.* Table A). The sequence of the dielectric

TABLE A.

(Specific rotations with reference to Hg_{5461}—line are recorded in this table).

Structural formula.		1*	2	3	4	5	6	Solvents in order of decreasing rotatory power.
Solvent...		Benzene.	Chloroform.	Pyridine.	Acetone.	Ethyl alcohol.	Methyl alcohol.	
Dielectric constant...		2·28	5·2	12·4	21·5	25·8	31·2	
C_8H_{14} 	$[\alpha]$	367·1	424·6	433·2	448·9	451·3	480·0	6>5>4>3>2>1
	λ_0	0·3250	0·3360	0·3330	0·3359	0·3422	0·3425	
C_8H_{14} 	$[\alpha]$	352·6	384·8	405·8	442·3	439·9	454·4	6>4>5>3>2>1
	λ_0	0·3090	0·3467	0·3148	0·3347	0·3335	0·3366	
C_8H_{14} 	$[\alpha]$	355·4	401·6	401·6	425·8	440·8	465·0	6>5>4>3>2>1
	λ_0	0·3317	0·3356	0·3356	0·3365	0·3412	0·3555	
C_8H_{14} 	$[\alpha]$	361·8	393·0	389·7	418·3	423·0	430·0	6>5>4>2>3>1
	λ_0	0·3466	0·3445	0·3763	0·3718	0·3724	0·3788	
C_8H_{14} 	$[\alpha]$	331·3	388·6	398·6	417·1	428·0	445·7	6>5>4>3>2>1
	λ_0	0·3273	0·3439	0·3626	0·3463	0·3464	0·3824	
		Un†> $p>m$; $\alpha>\beta$	Un> $p>m$; $\alpha>\beta$	Un> $m>p$; $\beta>\alpha$	Un> $m>p$; $\alpha>\beta$	Un> $m>p$; $\beta>\alpha$	Un> $p>m$; $\beta>\alpha$	

* The numbers refer to the solvent as given against each at the head of the table.

† Unsubstituted anilino-compound

constants of the solvents is also the same. The graphs of rotatory dispersion of *m*-toluidinomethylene-*d*-camphor (Fig. I) in different solvents, which do not intersect, show that the relationship holds for other wavelengths also. The same is the case for other compounds except for α-naphthylaminomethylenecamphor, the graphs of which for pyridine and chloroform intersect; so that the order for rotatory power given above is inverted for wave-lengths smaller than that for mercury green (*cf.* Tables XIX and XX, XXV and XXVI). The graphs for the remaining four compounds are not reproduced.

The Influence of Substituents on the Rotatory Power of the Position Isomerides.—It is seen from Table A that the sequence of the rotatory power of the position isomerides is, unsubstituted$\geq p \geq m$ in benzene, chloroform and methyl alcohol, whereas in the remaining three solvents the sequence becomes unsubstituted$> m > p$. This is neither in agreement with Frankland's lever-arm hypothesis (Frankland and Wharton, *J. Chem. Soc.*, 1896, **69**, 1583), nor with the electrostatic modification suggested by Rule (*J. Chem. Soc.*, 1924, **125**, 1122). The unsubstituted compound has the highest rotatory power, but this is opposed to both the views. The change in the sequence of rotatory power with the nature of the solvent in the above mentioned instances, as well as in those of α- and β-naphthylaminomethylenecamphors (Table A) are also facts which cannot be accommodated on these hypotheses. These are brought out in a still more striking manner by comparing the graphs of rotatory dispersion of *m*- and *p*-toluidinomethylenecamphors in methyl alcohol, (Fig. I, graphs 6 and 7). It is seen that the *meta*- and *para*-isomerides intersect at wave-length corresponding to that of Na_D so that for wave-lengths smaller than 5893 Å. U., the sequence is $p \geq m$, and for wave-lengths greater than 5893 Å. U., it is reversed. Incidentally this brings out the importance of the study of rotatory dispersion in such investigations instead of deducing the effect of constitution on rotatory power from observations confined to a single wave-length (*cf.* Singh and Bhaduri, *J. Indian Chem. Soc.*, 1930, **7**, 774).

The Effect of Unsaturated Conjugation on Rotatory Power.—The *aryl* derivatives of aminomethylenecamphor from an intermediate series of compounds to the corresponding derivatives of imino- and amino-camphor, and are well suited for illustrating the effect of conjugated double bonds on rotatory power. A comparison

Rotatory Dispersion of m-*Toluidinomethylene*-d-*camphor* (1—6).

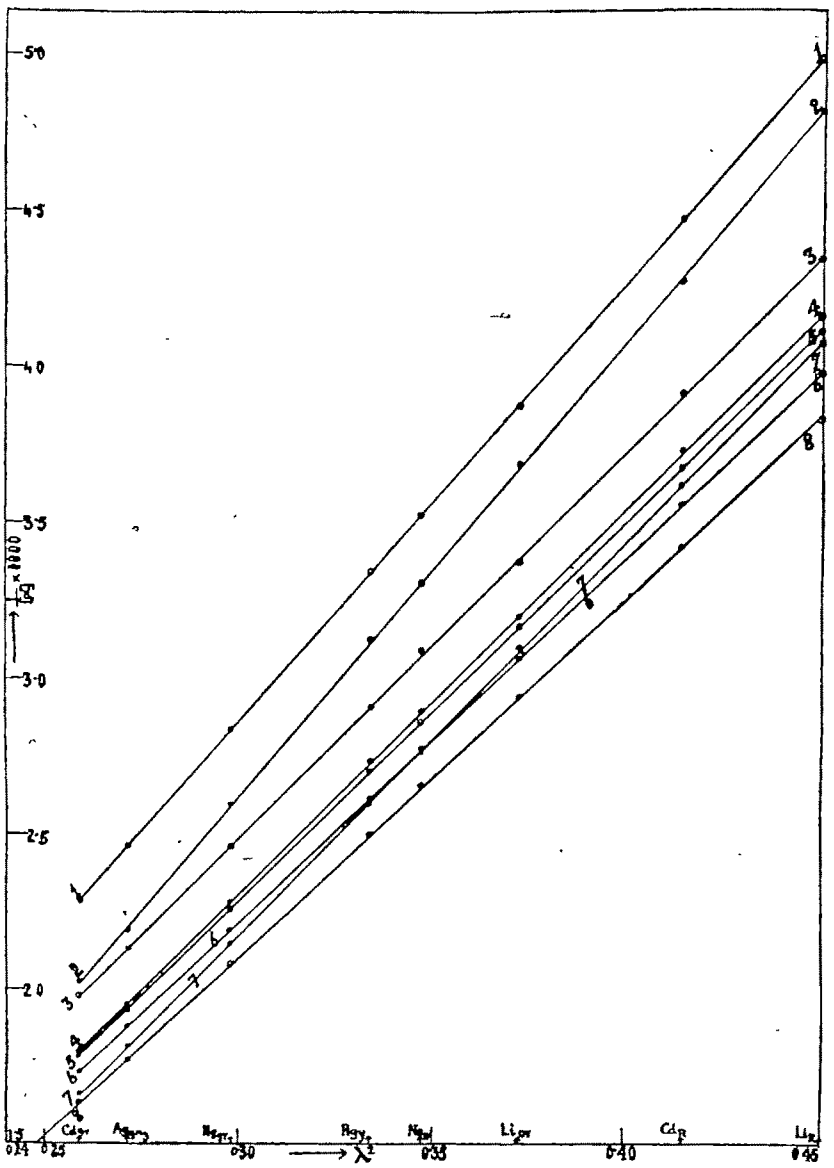
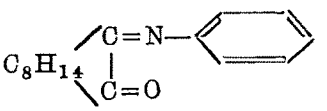


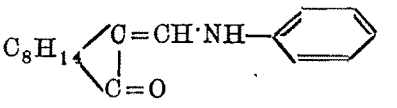
Fig. 1.

1—Benzene; 2—Chloroform; 3—Pyridine; 4—Ethyl alcohol; 5—Acetone; 6—Methyl alcohol.

of the structural formulae of the phenyl derivatives of the three series of compounds and the phenylhydrazone of camphorquinone and their rotatory power in chloroform brings out this effect in a striking manner:

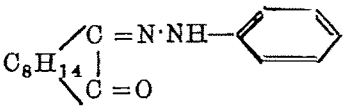
1. 

$[M]_{Na_D} = 1597°$

2. 

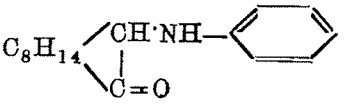
$[M]_{Na_D} = 854.3°$

(Singh, Mallick and Bhaduri, *loc. cit.*)

3 

$[M]_{Na_D} = 832°$

(Forster and Thornley, *J. Chem. Soc.*, 1909, **95**, 947).

4. 

$[M]_{Na_D} = 299{\cdot}7°$

(Singh, Mallick and Bhaduri, *loc. cit.*).

This comparison brings out the enhanced effect on rotatory power of the phenyl group when acting in conjunction with the azethenoid group, and the remarkable fall in the value of the rotatory power when this conjugation is broken (1 and 4). When the phenyl group is not in proximity of the asymmetric centre but is divorced from it by the interposition of other groups so that the conjugation is broken, the rotatory power is also considerably depressed (1 and 2 ; 1 and 3). Lastly the above parallel shows that the auxorotatory effect of the carbon-carbon and carbon-nitrogen linkings is very nearly the same (2 and 3).

A similar relationship is revealed by the remaining four series of compounds.

The Physical Identity of Enantiomers.—According to Pasteur's principle of molecular dissymmetry, the *d* and *l* forms are represented as true mirror images of one another, differing in sign, but absolutely identical in the numerical value of the rotatory power. The numerical values of the rotatory power of the two forms (Tables I—XXXVI) further support this fundamental principle which has received ample proof of its validity in the previous parts of these investigations.

The individual readings of the angle of rotation did not differ from the mean by more than 0·02°. A calculation from the tables of rotatory dispersion will show that the maximum errors obtained by working out the effect on the result of the maximum deviation (0·02°) are generally well within the attainable limits of experimental accuracy.

Out of 297 observations of *dextro*- and *laevo*-rotations which are now recorded, only in the case of α-naphthylaminomethylene-*d*-camphor in ethyl alcohol for Hg_{5780}, the specific rotatory powers of the two optically active forms differ by 4·3° (Table XXIII) which corresponds to a difference of 0·035° in the observed angle of rotation, which is slightly greater than the maximum deviation (0·02°) allowed. The remaining three cases, in which the deviation in the observed angle of rotation corresponds to about 0·03°, are those of anilinomethylenecamphor in acetone for Hg_{4358} (Table V), α-naphthylaminomethylenecamphor in methyl alcohol for Cd_{5085} (Table XXVIII) and β-naphthylaminomethylenecamphor in pyridine for Ag_{5209} (Table XXIII). Besides the four cases mentioned above, there are only about ten other instances in which the differences correspond to variations in the observed angle of rotation lying between 0·02° and 0·03°. In all other cases this variation is less than 0·02°. All these are, however, of the nature of casual experimental errors.

The melting points of the racemic forms of *p*-toluidinomethylenecamphor and β-naphthylaminomethylenecamphor are higher than those of the optically active forms. These forms are true *dl*-compounds, at least in the solid state.

Experimental.

The *laevo*- and the *racemic* compounds described in the present paper were prepared in the same way as the corresponding *dextro*-isomers and had the same crystalline form and similar solubility.

Anilinomethylene-d-*camphor* was prepared by the method of Bishop, Claisen and Sinclair (*loc. cit.*) and has the same crystalline form but melts at 158-160° instead of 167-170°. (Found: C, 79·84; H, 8·52; N, 5·57. $C_{17}H_{21}ON$ requires C, 80·00; H, 8·24; and N, 5·51 per cent.) *Anilinomethylene*-l-*camphor*, m. p. 158-160°. (Found: N, 5·51. $C_{17}H_{21}ON$ requires N, 5·51 per cent.). *Anilinomethylene*-dl-*camphor*, m. p. 135-136°. (Found: N. 5·58. $C_{17}H_{21}ON$ requires N, 5·51 per cent.)

m-*Toluidinomethylene*-d-*camphor* was prepared by mixing molecular proportions of oxymethylene-*d*-camphor in methyl alcohol and *m*-toluidine in glacial acetic acid and cooling the mixture in ice when a crystalline precipitate separated. It was crystallised from hot alcohol as colourless rectanglar plates melting at 149-150°. (Found: C, 79·95; H, 8·73. $C_{18}H_{23}ON$ requires C, 80·30; H, 8·55 per cent.). It is fairly soluble in most of the organic solvents. m-*Toluidinomethylene*-l-*camphor*, m. p. 149-150°. (Found: N, 5·36. $C_{18}H_{23}ON$ requires N, 5·20 per cent.). m-*Toluidinomethylene*-dl-*camphor*, m. p. 120°. (Found: N, 5·26. $C_{18}H_{23}ON$ requires N, 5·20 per cent.)

p-*Toluidinomethylene*-d-*camphor* was prepared by the method of Claisen and co-workers (*loc. cit.*) and has the same crystalline form but melts at 179-180° instead of 183-189°. (Found: C, 80·16; H, 8·76; N, 5·34. $C_{18}H_{23}ON$ requires C, 80·30; H, 8·55; N, 5·20 per cent.). p-*Toluidinomethylene*-l-*camphor*, m. p. 179-180°. (Found: N, 5·34. $C_{18}H_{23}ON$ requires N, 5·20 per cent.)

p-*Toluidinomethylene*-dl-*camphor*, faintly yellow needles, m. p. 186°. (Found: N, 5·35. $C_{18}H_{23}ON$ requires N, 5·20 per cent.).

α-*Napthylaminomethylene*-d-*camphor* exists in two dimorphous forms, α-form, m. p. 152°-154° and β-form, m. p. 76-78°.

α-*Form*: Oxymethylene-*d*-camphor (1·8 g.) dissolved in methyl alcohol was added to α-naphthylamine (1·6 g.) in glacial ascetic acid and cooled in ice, when, on vigorous scratching, a pale yellow product separated. It was washed with methyl alcohol till free from acetic acid (yield 80%). It melts at 152-154°. (Found: C, 82·16; H, 7·80; N, 4·79. $C_{21}H_{23}ON$ requires C, 82·56; H, 7·59; N, 4·59 per cent.). It is freely soluble in most of the organic solvents.

β-*Form*: On repeated crystallisation of the α-form from methyl alcohol, the β-form is obtained as pale yellow rectangular plates, m. p. 76-78°. The melting point of oxymethylenecamphor is depressed by the β-form while that of a mixture of the α- and β-forms is intermediate between the two. All attempts to convert the β-form into the α-form have failed. The conversion of the α-form to the β-form is accelerated by crystallisation from methyl alcohol with *prolonged digestion*. The presence of water is undesirable as it converts the product into an oil, which is very difficult to crystallise. (Found: C, 82·29; H, 7·80; N, 4·70. $C_{21}H_{23}ON$ requires C, 82·56; H, 7·59; N, 4·59 per cent.).

α-Naphthylaminomethylene-l-*camphor*, *α-form*, m.p. 151-153°. (Found: N, 4·71. $C_{21}H_{23}ON$ requires N, 4·59 per cent.). *β-form*, m.p. 76-78°. (Found: N, 4·60. $C_{21}H_{23}ON$ requires N, 4·59 per cent.).

α-Naphthylaminomethylene-dl-*camphor*, *α-form*, m.p. 140°-142° (Found: C, 82·26; H, 7·77; N, 4·76. $C_{21}H_{23}ON$ requires C, 82·56; H, 7·59; N, 4·59 per cent.). *β-form*, m.p. 88-90°. (Found: C, 82·24; H, 7·89; N, 4·74. $C_{21}H_{23}ON$ requires C, 82·56; H, 7·59; N, 4·59 per cent.).

β-Naphthylaminomethylene-d-*camphor* was prepared in the same way as that of Pope and Read (*loc. cit.*) and has the same melting point (184-87°) and crystalline form. (Found: N, 4·77. $C_{21}H_{23}ON$ requires N, 4·59 per cent.). *β-Naphthylaminomethylene*-l-*camphor*, m.p. 184-87°. (Found: N, 4·74. $C_{21}H_{23}ON$ requires N, 4·59 per cent.). *β-Naphthylaminomethylene*-dl-*camphor*, m.p. 187-89°. (Found: N, 4·75. $C_{21}H_{23}ON$ requires N, 4·59 per cent.).

The rotatory power determinations were made in a 2 dcm. jacketed tube at 35°. The value of λ_0, calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm.

TABLE I.

Anilinomethylenecamphor in Benzene.

$$[\alpha] = \pm \frac{70{\cdot}71}{\lambda^2 - 0{\cdot}1056}; \quad \lambda_0 = 0{\cdot}3250.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4004	836·8°	−1·7°	Hg_{4358}	±838·5°	−0·6°	−837·9°	0·4016
0·4000	568·8	+2·2	Cd_{4800}	566·6	±0	566·6	0·4024
,,	462·5	+0·7	Cd_{5086}	461·8	+0·4	462·2	,,
,,	427·5	+0·7	Ag_{5209}	426·8	−0·6	426·2	,,
0·4004	367·1	−0·1	Hg_{5461}	367·2	+1·3	368·5	0·4016
,,	309·7	+0·3	Hg_{5780}	309·4	+0·6	310·0	,,
,,	292·2	−0·4	Na_{5893}	292·6	−0·5	292·1	0·4040
,,	264·8	−0·1	Li_{6104}	264·9	±0	264·9	,,
0·4000	228·8	−0·1	Cd_{6438}	228·9	−0·2	228·7	0·4024
0·4004	204·8	−0·5	Li_{6708}	205·3	+0·1	205·4	0·4040

The solution exhibited mutarotation; the initial values $[\alpha]Hg_{5461} = 367{\cdot}1°$ and $[\alpha]Hg_{5780} = 309{\cdot}7°$ changing to 341·0° and

287·2° in course of 8 hours and to 316·0° and 266·0° respectively in course of 21 hours.

TABLE II.

Anilinomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{81{\cdot}21}{\lambda^2 - 0{\cdot}1109}; \quad \lambda_0 = 0{\cdot}3330.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] = o.	o−c.	Line.	Calc. [α] = c.	o′−c	Obs. [α] = o′.	Concn. g/100 c.c.
0·4040	548·3°	−1·2°	Cd_{5086}	±549·5°	+1·8°	−551·3°	0·4000
	507·4	+1·5	Ag_{5209}	505·9	−0·9	505·0	
	433·2	−0·4	Hg_{5461}	433·6	+0·2	433·8	
	363·9	±0	Hg_{5780}	363·9	−0·1	363·8	
	342·9	−0·7	Na_{5893}	343·6	+0·2	343·8	
	310·6	+0·3	Li_{6104}	310·3	−0·3	310·0	
	266·1	−1·4	Cd_{6438}	267·5	+0·3	267·8	
	240·1	+0·6	Li_{6708}	239·5	+0·5	240·0	

The solution did not exhibit any mutarotation

TABLE III.

Anilinomethylenecamphor in Ethyl Alcohol.

$$[\alpha] = \pm \frac{81{\cdot}83}{\lambda^2 - 0{\cdot}1171}; \quad \lambda_0 = 0{\cdot}3422.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] = o.	o−c.	Line.	Calc. [α] = c.	o′−c.	Obs. [α] = o′.	Concn. g/100 c.c.
0·4000	1126·3°	+2·3°	Hg_{4358}	±1124°	−1·0°	−1123·0°	0·4024
	720·0	−2·1	Cd_{4800}	722·1	−1·5	720·6	
	579·9	+2·0	Cd_{5086}	577·9	+1·1	579·0	
	531·3	+0·6	Ag_{5209}	530·7	+1·1	531·8	
	451·3	−0·6	Hg_{5461}	451·9	−0·9	451·0	
	377·5	+0·5	Hg_{5780}	377·0	+0·8	377·8	
	353·8	−1·4	Na_{5893}	355·2	−1·1	354·1	
	320·0	−0·2	Li_{6104}	320·2	+0·4	320·6	
	276·3	+1·2	Cd_{6438}	275·1	−0·5	274·6	
	245·6	−0·2	Li_{6708}	245·8	+0·2	246·0	

The solution did not exhibit mutarotation.

TABLE IV.

Anilinomethylenecamphor in Chloroform.

$$[\alpha] = \pm\frac{78{\cdot}57}{\lambda^2-0{\cdot}1129}; \qquad \lambda_0 = 0{\cdot}3360.$$

Dextro					*Lævo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c
0·4016	1028·0°	+2·0°	Hg_{4358}	±1021·0°	−1·0°	−1020·0°	0·4040
	536·7	−2·4	Cd_{5086}	539·1	−0·5	538·6	
	494 3	−1·8	Ag_{5209}	496·1	+1·3	497·4	
	424·6	+0·6	Hg_{5461}	424·0	+0·5	424·5	
	356·1	+0·9	Hg_{5780}	355·2	±0	355·2	
	335·0	−0·3	Na_{5893}	335·3	−1·1	334·2	
	302·6	±0	Li_{6104}	302·6	−0·6	302·0	
	260·3	−0·2	Cd_{6438}	260·5	+0·6	261·1	
	234·1	+1·0	Li_{6708}	233·1	+0·9	234·0	

The solution did not exibit any mutarotation.

TABLE V.

Anilinomethylenecamphor in Acetone.

$$[\alpha] = \pm\frac{83{\cdot}08}{\lambda^2-0{\cdot}1128} \qquad \lambda_0 = 0{\cdot}3359.$$

Dextro					*Lævo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c
0·4032	1074·0°	−2·0°	Hg_{4358}	±1076·0	+1·8°	−1077·8°	0·4000
	704·5	−2·0	Cd_{4800}	706·5	−1·5	705·0	
	570 6	+1·0	Cd_{5086}	569·6	+0·4	570·0	
	525·9	+1·8	Ag_{5209}	524·1	+0·9	525·0	
	448·9	+0·1	Hg_{5461}	448·1	−0·6	447·5	
	375·2	−0·2	Hg_{5780}	375·4	−0·4	375 0	
	353·5	−0·8	Na_{5893}	354·3	+0·7	355·0	
	321·2	+1·4	Li_{6104}	319·8	−1·0	318·8	
	275·4	±0	Cd_{6438}	275·4	+0·9	276·3	
	245·5	−0·8	Li_{6708}	246·3	+0	246·3	

The solution did not exibit any mutarotation.

TABLE VI.

Anilinomethylenecamphor in Methyl Alcohol.

$$[\alpha] = \pm \frac{86{\cdot}78}{\lambda^2 - 0{\cdot}1178}; \qquad \lambda_0 = 0{\cdot}3425.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′	Concn. g/100 c.c.
0·4000	1197·5°	+2·5°	Hg_{4358}	±1195·0°	−1·0°	−1194·0°	0·4021
	765·0	−2·2	Cd_{4800}	767·2	−0·5	766·7	
	612·5	−1·3	Cd_{5086}	613·8	+1·3	615·1	
	565·0	+1·5	Ag_{5209}	563·5	+0·6	564·1	
	480·0	+0·3	Hg_{5461}	479·7	−1·3	478·4	
	400·0	−0·2	Hg_{5780}	400·2	−0·1	400·1	
	376·3	−1·0	Na_{5893}	377·3	+0·5	377·8	
	340·0	+0·1	Li_{6104}	339·9	+0·6	340·5	
	291·9	±0	Cd_{6438}	291·9	−1·2	290·7	
	261·3	+0·5	Li_{6708}	260·8	+0·1	260·9	

The solution did not exibit any mutarotation.

TABLE VII.

m-*Toluidinomethylenecamphor in Chloroform.*

$$[\alpha] = \pm \frac{68{\cdot}55}{\lambda^2 - 0\ 1202}; \qquad \lambda_0 = 0{\cdot}3467.$$

Dextro					*Laevo*		
Concn. g/100c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c	o′−c.	Obs [α] =o′.	Concn. g/100 c.c.
0·4016	493·1°	−1·8°	Cd_{5086}	±494·9°	+0·4°	−495·3°	0·4028
	455·7	+2·1	Ag_{5209}	453·6	−0·5	453·1	
	384·8	−0·3	Hg_{5461}	385·1	−0·2	384·9	
	320·2	−0·3	Hg_{5790}	320·5	+0·9	321·4	
	302·6	+0·5	Na_{5893}	302·1	+0·8	302·9	
	271·5	−0·1	Li_{6104}	271·6	+0·2	271·8	
	234·1	+1·1	Cd_{6438}	233·0	+0·4	233·4	
	206·7	−1·1	Li_{6708}	207·8	−1·7	206·1	

No mutarotation was observed even after 24 hours.

TABLE VIII.

m-Toluidinomethylenecamphor in Benzene.

$$[\alpha] = \pm \frac{71{\cdot}37}{\lambda^2 - 0{\cdot}0955}; \qquad \lambda_0 = 0{\cdot}3090.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′	Concn. g/100 c.c
0·4028	−436·9°	−0·4°	Cd_{5086}	±437·3°	+0·9°	−438·2°	0·4016
	405·8	−0·2	Ag_{5209}	406·0	−0·2	405·8	
	352·6	+0·5	Hg_{5461}	352·1	+0·6	352·7	
	299·2	+0·2	Hg_{5780}	299·0	−0·3	298·7	
	284·3	+0·7	Na_{5893}	283·6	+0·2	283·8	
	258·2	+0·7	Li_{6104}	257·5	−1·0	256·5	
	223·5	−0 3	Cd_{6438}	223·8	+0·3	224·1	
	201·1	−0·2	Li_{6708}	201·3	−0·8	200·5	

The solution exibited mutarotation; the initial value $[\alpha]\ Hg_{5461}$ =352·6° changing to 340·1° in course of 24 hours.

TABLE IX.

m-Toluidinomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{80{\cdot}48}{\lambda^2 - 0{\cdot}0991}; \qquad \lambda_0 = 0{\cdot}3148.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o.	Concn. g/100 c.c.
0·4016	503·0°	−1·2°	Cd_{5085}	±504·2°	+1·7°	−505·9°	0·4022
	468·2	−0·8	Ag_{5209}	467·4	−0 1	467·3	
	405·8	+1·6	Hg_{5461}	404·2	+0·8	405·0	
	343.7	+1·2	Hg_{5780}	342·5	+0 2	342 7	
	323·7	−0·8	Na_{5893}	324·5	−1·7	322 8	
	296·3	+2·0	Li_{6104}	294·3	−0·2	294·1	
	255·3	+0.1	Cd_{6438}	255·2	+0·3	255·5	
	230·4	+1·0	Li_{6708}	229·4	−0·1	229·3	

No mutarotation was observed even after 24 hours.

TABLE X.

m-Toluidinomethylenecamphor in Acetone.

$$[\alpha] = \pm\frac{82{\cdot}31}{\lambda^2-0{\cdot}1120}\ ;\quad \lambda_0 = 0{\cdot}3347.$$

Dextro					*Laevo*		
Concn. g/100c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concn. g/100 c.c
0·4024	559·1°	−1·9°	Cd_{5085}	±561·0°	−0·8°	−560·2°	0·4024
	515·6	−1·2	Ag_{5209}	516·8	+1·2	518·0	
	442·3	+0·2	Hg_{5461}	442·1	−0·1	442·0	
	372·5	+1·9	Hg_{5780}	370·6	−0·8	369·8	
	348·2	−1·9	Na_{5893}	350·1	+1·1	351·0	
	315·6	−0·3	Li_{6104}	315·9	+1·5	317·4	
	273·3	+1·1	Cd_{6438}	272·1	+0·5	272·6	
	244·8	+1·2	Li_{6708}	243·6	+0·4	244·0	

No mutarotation was observed even after 24 hours.

TABLE XI.

m-Toluidinomethylenecamphor in Methyl Alcohol.

$$[\alpha] = \pm\frac{85{\cdot}21}{\lambda^2-0{\cdot}1112}\ ;\quad \lambda_0 = 0{\cdot}3335.$$

Dextro					*Laevo*		
Concn. g/100c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concn. g/100 c.c.
0·4016	577·6°	±0°	Cd_{5085}	±577·6	+0·6	−578·2	0·4012
	532·9	+0·7	Ag_{5209}	532·2	+1·2	533·4	
	454·4	−1·3	Hg_{5461}	455·7	−0·9	454·8	
	383·5	+1·2	Hg_{5780}	382·3	+0·2	382·5	
	358·6	−2·6	Na_{5893}	361·2	+0·2	361·4	
	326·2	+0·2	Li_{6104}	326·0	−0·8	325·2	
	281·4	+0·4	Cd_{6438}	281·0	+1·9	282·9	
	251·5	± 0	Li_{6708}	251·5	−1·0	250·5	

No mutarotation was observed even after 24 hours.

TABLE XII.

m-*Toluidinomethylenecamphor in Ethyl Alcohol.*

$$[\alpha] = \pm\frac{81{\cdot}02}{\lambda^2-0{\cdot}1184} \qquad \lambda_0 = 0{\cdot}3366.$$

Dextro					*Laevo*		
Concn. g/100c.c.	Obs.[α] =o.	o−c.	Line.	Calc.[α] =c.	o′−c.	Obs.[α] =o′.	Concn. g/100 c.c.
0·4012	557·0°	−0·1	Cd_{5485}	±557·1°	+1·7°	−558·8°	0·4000
	513·5	+0·8	Ag_{5209}	512·7	−0·2	512·5	
	439·9	+1·2	Hg_{5461}	438·7	+1·6	440·3	
	365·2	−1·8	Hg_{5780}	367·0	−0·8	366·2	
	345·2	−1·3	Na_{5893}	346·5	+1·0	347·5	
	312·7	+0·3	Li_{6104}	312·4	± 0	312·4	
	267·8	−1·1	Cd_{6438}	268·9	−0·1	268·8	
	240·6	± 0	Li_{6708}	240·6	−0·6	240·0	

No mutarotation was observed even after 24 hours.

TABLE XIII.

p-*Toluidinomethylenecamphor in Ethyl Alcohol.*

$$[\alpha] = \pm\frac{80{\cdot}13}{\lambda^2-0{\cdot}1164}; \qquad \lambda_0 = 0{\cdot}3412.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs.[α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs.[α] =o′.	Concn. g/100 c. c.
0·4082	562·7°	−0·4°	Cd_{5086}	±563·1°	−0·6°	−562·5°	0·4000
	519·2	+2·0	Ag_{5209}	517·2	+0·3	517·5	
	440·8	±0	Hg_{5461}	440·8	−0·8	440·0	
	367·3	−0·8	Hg_{5780}	368·1	−0·6	367·5	
	349·8	+2·5	Na_{5893}	347·3	+1·5	348·8	
	311·3	−1·5	Li_{6104}	312·8	−0·3	312·5	
	269·0	+0·2	Cd_{6438}	268·8	−1·3	267·5	
	239·1	−1·0	Li_{6708}	240·1	+1·1	241·2	

The solution did not exhibit mutarotation.

TABLE XIV.

p-Toluidinomethylenecamphor in Methyl Alcohol.

$$[\alpha] = \pm \frac{79{\cdot}56}{\lambda^2 - 0{\cdot}1264}; \qquad \lambda_0 = 0{\cdot}3555.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100c.c.
0·4000	601·3°	±0°	Cd_{5086}	±601·3°	−0·5°	−600·8°	0·4056
	550·0	+1·1	Ag_{5209}	548·9	−0·2	548·7	
	465·0	−0·9	Hg_{5461}	465·9	−0·4	465·5	
	385·0	+2·0	Hg_{5780}	383·0	+0·6	383·6	
	360·0	−0·4	Na_{5893}	360·4	−0·5	359·9	
	322·5	−0·5	Li_{6104}	323·0	−0·2	322·8	
	276·3	+0·2	Cd_{6438}	276·1	+0·7	276·8	
	245·0	−0·9	Li_{6708}	245·9	−0·1	245·8	

The solution exhibited slight mutarotation; the initial values $[\alpha]Hg_{5461} = 465{\cdot}0°$ and $[\alpha]Hg_{5780} = 385{\cdot}0°$ changing to 456·3° and 378·8° respectively in course of 15 hours.

TABLE XV.

p-Toluidinomethylenecamphor in Acetone.

$$[\alpha] = \pm \frac{78{\cdot}77}{\lambda^2 - 0{\cdot}1132}; \qquad \lambda_0 = 0{\cdot}3365.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c. c.
0·4016	540·4°	−1·0°	Cd_{5086}	±541·4°	±0°	−541·4°	0·4036
	499·2	+1·0	Ag_{5209}	498·2	+1·0	499·2	
	425·8	±0	Hg_{5461}	425·8	+0·4	426·2	
	356·2	−0·5	Hg_{5780}	356·7	−1·2	355·5	
	337·6	+1·0	Na_{5893}	336·6	+0·4	337·0	
	305·1	+1·4	Li_{6104}	303·7	−0·2	303·5	
	260·2	−1·2	Cd_{6438}	261·4	−1·3	260·1	
	234·1	+0·1	Li_{6708}	234·0	+8·2	234·2	

The solution did not exhibit mutarotation; but turned light pink on keeping.

TABLE XVI.

p-*Toluidinomethylenecamphor in Pyridine.*

$$[\alpha] = \pm \frac{74{\cdot}15}{\lambda^2 - 0{\cdot}1126}\ ; \qquad \lambda_0 = 0{\cdot}3356.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. $[\alpha]$ $=o.$	$o-c.$	Line.	Calc. $[\alpha]$ $=c.$	$o'-c.$	Obs. $[\alpha]$ $=o.$	Concn. g/100 c.c.
0·4008	505·4°	−2·1	Cd_{5086}	±507·5°	−1·7°	−505·8°	0·4040
	401·6	+2·1	Hg_{5461}	399·5	+0·2	399·7	
	335·5	+0·8	Hg_{5780}	334·7	−0·5	334·2	
	316·9	+1·0	Na_{5893}	315·9	−0·3	315·6	
	284·4	−0·8	Li_{6104}	285·2	+0·7	285·9	
	247·0	+1·4	Cd_{6438}	245·6	+0·7	246·3	
	218·3	−1·5	Li_{6708}	219·8	−0·7	219·1	

The solution did not exhibit mutarotation but turned scarlet red in course of two hours.

TABLE XVII.

p-*Toluidinomethylenecamphor in Benzene.*

$$[\alpha] = \pm \frac{66{\cdot}65}{\lambda^2 - 0{\cdot}1100}\ ; \qquad \lambda_0 = 0{\cdot}3317.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. $[\alpha]$ $=o.$	$o-c.$	Line.	Calc. $[\alpha]$ $=c.$	$o'-c.$	Obs. $[\alpha]$ $=o'.$	Concn. g/100 c.c.
0·4024	447·3°	−0·9°	Cd_{5086}	±448·2°	+0·6°	−448·8°	0·4000
	411·2	−2·0	Ag_{5209}	413·2	−0·7	412·5	
	355·4	+1·3	Hg_{5461}	354·1	−0·3	353·8	
	298·2	+0·7	Hg_{5780}	297·5	±0	297·5	
	280·8	−0·3	Na_{5893}	281·1	+0·2	281·3	
	254·8	+1·0	Li_{6104}	253·8	−1·3	252·5	
	220·0	+1·1	Cd_{6438}	218·9	+1·1	220·0	
	195·1	−0·9	Li_{6708}	196.0	−1·0	195·0	

The solution exhibited mutarotation, $[\alpha]_D$ =280·8° changing to 275° and to 250° in course of 1 hour and 15 hours respectively.

TABLE XVIII.

Toluidinomethylenecamphor in Chloroform.

$$[\alpha] = \pm \frac{74{\cdot}15}{\lambda^2 - 0{\cdot}1126} \; ; \qquad \lambda_0 = 0{\cdot}3556.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4008	505·4°	−2·1°	Cd_{5086}	±507·5°	−0·5°	−507·0°	0·4024
,,	467·8	+0·6	Ag_{5209}	467·2	+1·2	468 4	,,
,,	401·6	+2·1	Hg_{5461}	399·5	+0·5	400·0	,,
,,	335·5	+0·8	Hg_{5780}	334·7	+0·8	335·5	,,
,,	315·6	−0·3	Na_{5893}	315·9	−0·3	315 6	,,
,,	284·4	−0·8	Li_{6104}	285·2	+0·6	285·8	,,
,,	245·8	+0·1	Cd_{6439}	245·6	−0·1	245·5	,,
,,	218·3	−1·5	Li_{6708}	219·8	+0·2	220 0	,,

The solution exhibited mutarotation, the initial values $[\alpha]Hg_{5461} = 401{\cdot}6°$ and $[\alpha]Hg_{5780} = 335{\cdot}5°$ changing to 328·2° and 278·2° respectively in course of 30 hours.

TABLE XIX.

α-Naphthylaminomethylenecamphor (α-Form) in Chloroform.

$$[\alpha] = \pm \frac{70{\cdot}45}{\lambda^2 - 0{\cdot}1185} \; ; \qquad \lambda_0 = 0{\cdot}3445.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4020	501·0°	−1·5°	Cd_{5085}	±502·5°	±0°	−502·5°	0·4020
	462·6	+1·4	Ag_{5209}	461·2	−0·2	461·4	
	393·0	−1·0	Hg_{5461}	392·0	+1 0	393·0	
	328·5	−1 7	Hg_{5780}	326·8	+1·7	328 5	
	307·1	+1·0	Na_{5893}	308·1	−0·3	308·4	
	278·6	+1·3	Li_{6104}	277 3	+2·5	279·8	
	237·9	+0·1	Cd_{6438}	238·0	+0·7	238·7	
	212·7	−0·1	Li_{6708}	212·6	+1·3	213·9	

No mutarotation was observed even after 24 hours.

TABLE XX.

α-Naphthylaminomethylenecamphor (α-Form) in Pyridine

$$[\alpha] = \pm \frac{61{\cdot}28}{\lambda^2 - 0{\cdot}1416} \; ; \qquad \lambda_0 = 0{\cdot}3763.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4004	522·0°	−0·1°	Cd_{5085}	±522·1°	+0·9°	−523·0°	0·4008
	——	——	Ag_{5209}	472·3	+1·8	470·5	
	389 7	−1·7	Hg_{5461}	391·4	+0·6	392·0	
	388·4	+1·0	Ag_{5469}	389·4	——	——	
	317·2	—1·3	Hg_{5780}	318·5	+1·0	319·5	
	299·7	+1·5	Na_{5893}	298·2	+1·4	299·6	
	266·0	+0·6	Li_{6104}	265·4	+1·7	267·1	
	224·9	—0·4	Cd_{6438}	224·5	+1·4	225·9	
,,	198·6	—0·1	Li_{6708}	198·7	—0·2	198·5	

No mutarotation was observed even after 24 hours.

TABLE XXI.

α-Naphthylaminomethylenecamphor (α-Form) in Benzene.

$$[\alpha] = \pm \frac{64{\cdot}78}{\lambda^2 - 0{\cdot}1201} \; ; \qquad \lambda_0 = 0{\cdot}3465.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4008	469·1°	−0·3°	Cd_{5085}	±469·4°	−0·5°	−468·9°	0·4020
	428·4	±0	Ag_{5209}	428·4	−1.4	426·6	
	361·8	−1·9	Hg_{5461}	363·7	−0·6	363·1	
	359·3	−1·8	Ag_{5469}	361·1	...	...	
	305·1	+1·6	Hg_{5780}	303·5	+2·4	305.9	
	288·2	+1·8	Na_{5893}	286.4	+2·1	288·5	
	257·1	+0·6	Li_{6104}	256·5	−0·2	256·3	
	217·4	−2·3	Cd_{6438}	219·7	−0·8	218·9	
	197·2	+0·9	Li_{6708}	196·3	+1·4	197.7	

Mutarotation was observed after 24 hours ; the initial value $[\alpha]_{Hg_{5461}} =$ 361·8° changing to 340·6°

TABLE XXII.

α-Naphthylaminomethylenecamphor (α-Form) in Methyl Alcohol.

$$[\alpha] = \pm\frac{68{\cdot}41}{\lambda^2-0{\cdot}1397}\ ; \qquad \lambda_0 = 0{\cdot}3738.$$

Dextro					*Laevo*		
Concn. g/100 c. c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4000	573·6°	−1·4°	Cd_{5085}	±575·0°	+1·5°	−576·5°	0·4016
	522·5	+2·5	Ag_{5039}	520·0	+1·7	521·7	
	430·0	−1·6	Hg_{5461}	431·6	−0·8	430·8	
	353·7	+1·7	Hg_{5780}	352·0	+0·4	352·4	
	332·5	+2·5	Na_{5893}	330·0	+1·2	331·2	
	290·0	−2·1	Li_{6104}	292·1	−0·7	291·4	
	248·8	−0·1	Cd_{6438}	248·9	+0·1	249·0	
	220·0	+0·5	Li_{6708}	220·5	−1·1	220·4	

No mutarotation was observed even after 20 hours.

TABLE XXIII.

α-Naphthylaminomethylenecamphor (α-Form) in Ethyl Alcohol.

$$[\alpha] = \pm\frac{67{\cdot}74}{\lambda^2-0{\cdot}1387}\ ; \qquad \lambda_0 = 0{\cdot}3724.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c	Obs. [α] =o′.	Concn. g/100 c.c.
0·4008	563·9°	+0·6°	Cd_{5086}	±563·3°	+1.7°	−565·0	0·4000
,,	512·7	+1·7	Ag_{5208}	511·0	−1·0	510·0	
,,	423·0	−1·7	Hg_{5461}	424·7	−0·9	423·8	
,,	420·5	−2·2	Ag_{5469}	422·7	—	—	
,,	349·3	+2·6	Hg_{5780}	346·7	−1·7	345·0	
,,	322·8	−2·3	Na_{5893}	325·1	−2·6	322·5	
,,	292·0	+2·4	Li_{6104}	289·6	+0·4	290·0	
,,	245·8	+0·2	Cd_{6438}	245·6	+1·9	247·5	
,,	217·1	−0.5	Li_{6708}	217·6	+1·2	218·7	

No mutrotation was observed even after 24 hours.

TABLE XXIV.

α-Naphthylaminomethylenecamphor (α-Form) in Acetone.

$$[\alpha] = \pm\frac{67{\cdot}05}{\lambda^2-0{\cdot}1382}; \qquad \lambda_0 = 0{\cdot}3717.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4016	556·5°	−1·3°	Cd_{5085}	±557·8°	+0·6°	−558·4°	0·4012
	505·5	+1·8	Ag_{5209} –	503·7	+1·1	504·8	
	418·3	−0·8	Hg_{5461}	419·1	+0·9	420·0	
	341·2	−1·1	Hg_{5780}	342·3	−0·8	341·5	
	322·5	+1·5	Na_{5893}	321·0	+0·5	321·5	
	285·1	−0·9	Li_{6104}	286·0	−1·9	284·1	
	241·5	−1·2	Cd_{6438}	242·7	+0·3	243·0	
	215·4	+0·3	Li_{6708}	215·5	−1·2	214·3	

As the solution turns dark red on keeping it was not possible to examine the same for mutarotation.

TABLE XXV.

α-Naphthylaminomethylenecamphor (β-Form) in Chloroform.

$$[\alpha] = \pm\frac{71{\cdot}94}{\lambda^2-0{\cdot}1161}; \qquad \lambda_0 = 0{\cdot}3407.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs [α] =o′.	Concn. g/100 c.c.
0·4020	502·5°	−2.0°	Cd_{5085}	±504·5°	−0·8°	−503·7°	0·4006
	465·3	+1·9	Ag_{5209}	463·4	+1·5	464·9	
	398·2	+2·2	Hg_{5461}	396·0	+1·4	397·4	
	330·9	+0·9	Hg_{5780}	330·0	±0	330·0	
	310·9	−0·4	Na_{5893}	311·3	−1·3	310·0	
	279·8	−0·6	Li_{6104}	280·4	−1·6	278·8	
	242·5	+1·1	Cd_{6438}	241·4	−0·1	241·3	
	215·1	−0·4	Li_{6708}	215·5	−0·5	215·0	

No mutarotation was observed even after 24 hours.

TABLE XXVI.

α-Naphthylaminomethylenecamphor (β-Form) in Pyridine.

$$[\alpha] = \pm\frac{61{\cdot}94}{\lambda^2 - 0{\cdot}1418}\ ; \qquad \lambda_0 = 0{\cdot}3759.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4012	525·8°	−1·8°	Cd_{5085}	±527·6°	−0·2°	−527·4°	0·4020
	478·2	+1·6	Ag_{5209}	476·6	−0·3	476·8	
	392·3	−2·5	Hg_{5461}	394·8	+0.7	395·5	
	319·0	−2·2	Hg_{5780}	321·2	−0·3	320·9	
	300·3	−0 6	Na_{5893}	300·9	+0·1	301·0	
	266·7	−1·1	Li_{6104}	267·8	−1·7	266·1	
	228·1	+1·3	Cd_{6438}	226·8	+0·3	227·6	
	199·3	−1·9	Li_{6708}	201·2	−0·9	200·3	

No mutarotation was observed even after 24 hours.

TABLE XXVII.

α-Naphthylaminomethylenecamphor (β-Form) in Benzene.

$$[\alpha] = \pm\frac{65{\cdot}70}{\lambda^2 - 0{\cdot}1191}\ ; \qquad \lambda_0 = 0{\cdot}3451.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4004	470·8°	−0·1°	Cd_{5085}	±470·7°	+1·0°	−471 7°	0·4012
	430·8	−0·9	Ag_{5209}	431·7	+0·7	432 4	
	364·7	−2·0	Hg_{5461}	366·7	−1·5	365·2	
	304 7	−0·9	Hg_{5780}	305·6	−0·2	305·4	
	289·7	+1·6	Na_{5893}	288·1	−0·2	287·9	
	257·3	−1·9	Li_{6104}	259·2	+0·1	259·3	
	221·1	−1·3	Cd_{6438}	222 4	+0·7	223·1	
	198·6	±0	Li_{6708}	198·6	−0·8	199·4	

No mutarotation was observed even after 24 hours.

TABLE XXVIII.

α-Naphthylaminomethylenecamphor (β-Form) in Methyl Alcohol.

$$[\alpha] = \pm\frac{68{\cdot}44}{\lambda^2 - 0{\cdot}1404}\ ; \qquad \lambda_0 = 0{\cdot}3747.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4008	576·4°	−2·2°	Cd_{5085}	±578·6°	+1·4°	−580·0°	0·4000
	522·7	−0·4	Ag_{5209}	523·1	−1·8	521·3	
	432·9	−0·9	Hg_{5461}	433·8	−1·3	432·5	
	354·6	+1·3	Hg_{5780}	353·3	−0·8	352·5	
	333·1	+1·9	Na_{5893}	331·2	+1·4	332·6	
	293·2	−1·6	Li_{6104}	294·8	+0·2	295·0	
	249·5	−0·2	Cd_{6438}	249·7	+0·3	250·0	
	222·1	+0·9	Li_{6708}	221·2	+0·1	221·3	

No mutarotation was observed even after 24 hours.

TABLE XXIX.

α-Naphthylaminomethylenecamphor (β-Form) in Ethyl Alcohol.

$$[\alpha] = \pm\frac{68{\cdot}18}{\lambda^2 - 0{\cdot}1380}\ ; \qquad \lambda_0 = 0{\cdot}3715.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4008	568·9°	−0·6°	Cd_{5085}	±564·5°	+1·7°	−566·2°	0·4000
	512·7	+0·7	Ag_{5209}	512·0	+0·5	512·5	
	428·0	−2·0	Hg_{5461}	425·0	±0	425·0	
	348·1	+0·7	Hg_{5780}	347·4	+0·1	347·5	
	328·2	−2·6	Na_{5893}	325·8	−2·0	323·8	
	292·0	+1·6	Li_{6104}	290·4	+0·9	291·3	
	247·1	+0·7	Cd_{6438}	246·4	+1·1	247·5	
	218·8	±0	Li_{6708}	218·8	−0·8	217·5	

TABLE XXX.

α-Naphthylaminomethylenecamphor (β-Form) in Acetone

$$[\alpha]+ \pm \frac{68{\cdot}33}{\lambda^2-0{,}1354.}\ ; \qquad \lambda_0=0{\cdot}3680.$$

Dextro				*Laevo*			
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4012	554·6°	+0·4°	Cd_{5085}	±554·2°	±1·1°	−555·3°	·4008
	503·8	+1·0	Ag_{5209}	502·8	±0	502·8	
	418·9	−0·9	Hg_{5461}	419·8	+0·7	420·5	
	342·7	−1·1	Hg_{5780}	343·8	+0·5	344·3	
	322·6	−0·5	Na_{5893}	323·1	+1·1	324·4	
	286·6	−1·4	Li_{6104}	288 0	−0·2	288 2	
	244·3	−0·5	Cd_{6438}	244·8	−0 2	244·6	
	216·8	−0·4	Li_{6708}	217·2	−0·1	217·1	

The solution turned dark red on keeping.

TABLE XXXI.

β-Naphthylaminomethylenecamphor in Ethyl Alcohol.

$$[\alpha] = \pm\frac{78{\cdot}55}{\lambda^2-0{\cdot}1145}; \qquad \lambda_0 = 0{\cdot}3324.$$

Dextro				*Laevo*			
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4008	546·5°	+1·3°	Cd_{5086}	±545·2°	−1·5°	−543·7°	0·4000
	500·2	−0·9	Ag_{5209}	501·1	−1·1	500·0	
	428·0	+0·3	Hg_{5461}	427·7	−0·2	427·5	
	356·9	−0·8	Hg_{5780}	357·7	−0·2	357·5	
	336·9	−0·9	Na_{5893}	337·8	−0·3	337·5	
	304·3	−0 1	Li_{6104}	304·4	+0·6	305·0	
	234·6	+0·4	Li_{6708}	234·2	−0·4	233·8	

The solution did not exhibit mutarotation.

TABLE XXXII.

β-Naphthylaminomethylenecamphor in Methyl Alcohol.

$$[\alpha] = \pm\frac{79{\cdot}14}{\lambda^2 - 0{\cdot}1200}; \qquad \lambda_0 = 0{\cdot}3464.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs [α] =o′.	Concn. g/100 c.c.
0·4028	571·1°	+0·5°	Cd_{5086}	±570·6°	+0·7°	−571·3°	0·4000
	521·3	−1·7	Ag_{5209}	523·0	−1·7	521·3	
	445·7	+1·6	Hg_{5461}	444·1	+2·2	446·3	
	371·2	+1·5	Hg_{5780}	369·7	+0·3	370·0	
	348·8	+0·3	Na_{5893}	348·5	−1·0	347·5	
	314·1	−0·5	Li_{6104}	314·6	+0·4	315·0	
	268·1	−0·6	Cd_{6438}	268·7	−1·2	267·5	
	240·8	+1·0	Li_{6708}	239·8	+0·2	240·0	

The solution did not exhibit mutarotation.

TABLE XXXIII.

β-Naphthylaminomethylenecamphor in Pyridine.

$$[\alpha] = \pm\frac{66{\cdot}76}{\lambda^2 - 0{\cdot}1315}; \qquad \lambda_0 = 0{\cdot}3626.$$

Dextro					*Laevo*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4052	528·1°	+3·8°	Cd_{5086}	±524·8°	+1·2°	−526·0°	0·4020
	479·9	+2·4	Ag_{5209}	477·5	−1·2	476·3	
	398·6	−1·9	Hg_{5461}	400·5	−1·3	399·2	
	329·5	±0	Hg_{5780}	329·5	−1·2	328·3	
	309·7	+0·1	Na_{5893}	309·6	±0	309·6	
	275·2	−1·7	Li_{6104}	276·9	+0·4	277·3	
	236·9	+1·0	Cd_{6438}	235·9	+0·4	236·3	
	209·7	+0·1	Li_{6708}	209·6	−0·7	208·9	

The solution did not exhibit any mutarotation.

TABLE XXXIV.

β-Naphthylaminomethylenecamphor in Acetone.

$$[\alpha] = \pm\frac{74{\cdot}57}{\lambda^2-0{\cdot}1199}; \qquad \lambda_0 = 0{\cdot}3463.$$

Dextro				*Laevo*			
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4028	540·0°	+2·8°	Cd_{5086}	+537·2°	+1·6°	−538·8°	0·4000
	495·3	+2·7	Ag_{5209}	492·6	+2·4	495·0	
	417·1	−1·2	Hg_{5461}	418·3	−0·8	417·5	
	346·3	−1·8	Hg_{5780}	348·1	−0·6	347·5	
	326·5	−1·8	Na_{5893}	328·3	+0·5	328·8	
	295·4	+0·3	Li_{6104}	295·1	+1·2	296·3	
	225·9	±0	Li_{6708}	225·9	−0·9	225·0	

The solution did not exhibit mutarotation,

TABLE XXXV.

β-Naphthylaminomethylenecamphor in Chloroform.

$$[\alpha] = \pm\frac{69{\cdot}66}{\lambda^2-0{\cdot}1183}; \qquad \lambda_0 = 0{\cdot}3439.$$

Dextro				*Laevo*			
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4040	492·5°	−4·1°	Cd_{5086}	±496·6°	−2·1°	−494·5°	0·4024
	455·4	+0·1	Ag_{5209}	455·3	+0·7	456·0	
	388·6	+1·2	Hg_{5461}	387·4	+1·5	388·9	
	325·6	+2·8	Hg_{5780}	322·8	+1·5	324·3	
	307·0	+2·5	Na_{5893}	304·5	+1·1	305·6	
	278·5	−0·4	Li_{6104}	278·9	−0·6	278·3	
	235·2	±0	Cd_{6438}	235·2	—	—	
	210·4	+0·4	Li_{6708}	210·0	−1·3	208·7	

The solution exhibited slight mutarotation, $[\alpha]Hg_{5461}=388{\cdot}6°$ and $[\alpha]Hg_{5780}=325{\cdot}6°$ changing to 381·5° and 315·6° respectively in course of 24 hours.

TABLE XXXVI.

β-Naphthylaminomethylenecamphor in Benzene.

$$[\alpha] = \pm \frac{63{\cdot}14}{\lambda^2 - 0{\cdot}1071}; \quad \lambda_0 = 0{\cdot}3273.$$

Dextro					*Laeve*		
Concn. g/100 c.c.	Obs. [α] =o.	o−c.	Line.	Calc. [α] =c.	o′−c.	Obs. [α] =o′.	Concn. g/100 c.c.
0·4000	417·5°	+1·0°	Cd_{5086}	±416·5°	−0·6°	415·9°	0·4040
	383·8	−0·8	Ag_{5209}	384·6	−0·9	383·7	
	331·3	+0·8	Hg_{5461}	330·5	±0	330·5	
	278·8	+0·6	Hg_{5780}	278·2	+0·3	278·5	
	263 8	+1·0	Na_{5893}	262·8	−0·5	262·3	
	237·5	−0 4	Li_{6104}	237·9	±1·0	238·9	
	206·3	+0·9	Cd_{6438}	205·4	±0	205·4	
	182·5	−1·7	Li_{6708}	184·2	−1·0	183·2	

The solution exhibited slight mutarotation,

We wish to make grateful acknowledgement to the Government of Bihar and Orissa in the Ministry of Education for the grant of research scholarships to two of us (B. B. and T. B.) which have enabled them to take part in this investigation. We also wish to acknowledge the valuable assistance which we received from Babu Indramani Mahanti, B.Sc., the Head Assistant of the Chemical Department.

THE CHEMICAL LABORATORY,
RAVENSHAW COLLEGE, CUTTACK.

Received April 8, 1931.

Colloidal Chemical Analysis. Part I.

By Jnanendranath Mukherjee, Satyaprasad Roychoudhury and Mohinimohan Biswas.

General Introduction.

The present series aims at dealing with the theoretical relationships implied in customary interpretations of results from colloid chemical analysis of inorganic hydrosols. It is intended to deal mainly with the following aspects.—(1) Correlation of the cataphoretic speed with the chemical composition of the colloid and intermicellary liquid. The need for considering the adsorption of ions in detail for distinguishing between the presence of the ions on the solid and liquid sides of the interface and between electrical and primary adsorption of ions, have been emphasised by us (*Trans., Faraday Soc.*, 1921, **16**, 103; *Phil. Mag.*, 1922, **44**, 305; Chaudhury, *J. Indian Chem. Soc.*, 1926. **2**, 296; Chaudhury and Rai-Choudhuri, *ibid.*, 1927, **4**, 493; Rai-Chaudhuri and Bhattacharyya, *ibid.*, 1928, **5**, 735; *Kolloid Z.*, 1929, **49**, 362). (2) Measurements on the variation of the charge of colloidal particles in this laboratory show that it is not possible to speak of a *definite* critical coagulation potential independent of the method of preparation of the colloid, of the nature of the electrolyte, and of the degree of dilution (*loc. cit.*). The work of Weiser (*J. Phys. Chem.*, 1930, **44**, 101) has confirmed this conclusion. It has been shown (Rai-Choudhuri and Bhattacharyya, *loc. cit.*, see also Weiser, *loc. cit.*) that considerations of changes in the dielectric constant (Kruyt and Willigen, *Z. Phys. Chem.*, 1927, **130**, 170; *Kolloid Z.*, 1928, **44**, 22; Ghosh, *J. Chem. Soc.*, 1929, p. 2693) in the interfacial layer do not suffice to account for the differences in the cataphoretic speeds at the coagulating concentration. It has been contended that a definite critical coagulation potential exists for electrolytes having polyvalent coagulating ions, if not for those having univalent ones. In the following table are given the cataphoretic speeds at the coagulating concentration of arsenious sulphide under different conditions which show that there is no definite critical coagulation potential *even for divalent cations* (Kruyt and Willigen, *Z. Phys. Chem., loc. cit.*; Briggs, *J. Phys. Chem.*, 1930, **34**, 1326; Ghosh, *loc. cit.*).

TABLE I.

Sol.	Electrolyte and its conc.	Cataphoretic speed $\times 10^5$.	Reference.
Sample I.			
(Diluted 1 : 1)	·039 *N*-HCl (C_H = ·031 *N*)	45·0**	*J. Indian Chem. Soc.*, 1926, 2, 303.
,,	·111 *N*-Oxalic (C_H = ·0333 *N*)	36·3**	,,
,,	2·46 *N*-Formic (C_H = ·027 *N*)	34·7**	,,
,,	·1 *N*-Acetic (C_H = ·0012 *N*)	35·7**	,,
Sample II.			
(Diluted 1 : 1)	·001 *N*-$BaCl_2$ + ·1134 *N*-Sodium benzoate.	41	*J. Indian. Chem. Soc.*, 1927, 4, 508.
,,	·0015 *N*-Calcium benzoate + ·1134 *N*-Sodium benzoate.	36·2	,,
,,	·0015 *N*-Calcium benzoate.	9·1*	,,
,,	·001 *N*-$BaCl_2$ + ·0375 *N*-NaCl.	39·7**	,,
,,	·001 *N*-$BaCl_2$.	20·2*	,,
,,	·0015 *N*-$MgCl_2$ + ·0375 *N*-NaCl.	42·6**	,,
,,	·0015 *N*-$MgCl_2$ + ·04 *N*-LiCl.	50·4**	,,
,,	·0015 *N*-$MgCl_2$.	15·5*	
Sample III.			
(Diluted 1 : 1)	·056 *N*-KCl.	68.8	*J. Indian Chem. Soc.*, 1928, 5, 741.
(Diluted 1 : 5)	·067 *N*-KCl.	50·6	,,
(Diluted 1 : 10)	·077 *N*-KCl.	47·3	,,
Sample IV.			
(Diluted 1 : 1)	·055 *N*-KCl.	59·9	*Kolloid Z.*, 1930, 53, 160
,,	·001 *N*-$BaCl_2$.	14·84	,,

(3) In several instances (Rai-Choudhury and Bhattacharyya, *loc. cit.*) the coagulating concentration is not affected materially by the initial cataphoretic speed of the colloidal particle or the speed at coagulation and that in a number of cases the cataphoretic speed is

* Coagulation did not occur even at this low cataphoretic speed.

** Near the coagulating region.

different before and after coagulation. Excepting these measurements there are no reliable data in the literature dealing with the cataphoretic speed at coagulating concentrations and the observed time effect and further experimental data would be of interest. (4) The conditions for satisfactory measurements of the cataphoretic speed by the boundary method have been discussed by us (*loc. cit.*). It appears necessary to emphasise them again in relation to measurements which overlook them, because one cannot at all be sure that they are not erroneous. (5) Another point of interest is whether there is a relationship between the cataphoretic speed and the density of free electrical charges on the surface of colloidal particles. (6) In the usual interpretations of the observed reversible E. M. F. of ions in a colloidal solution the following aspect is overlooked and requires to be clearly formulated. It is not known whether the observed electromotive force (for example with a calomel electrode in a colloidal solution of ferric hydroxide containing chloride ions) is to be ascribed simply to the ions present (chlorine in this case) in the intermicellary liquid or to the free ions associated with the charged colloidal particles or to both. (7) Also in investigations on the effects of dilution of a sol on its properties, the theoretical dicussions rest upon too simple a picture and the complicated changes that result from dilution are not fully taken into consideration.

Ferric Hydroxide Hydrosol.—The present paper deals with ferric hydroxide hydrosols. As with previous workers, part of the information has to be obtained indirectly. The difficulties in the way of accepting the conclusions of previous investigators as also the need for direct methods will be pointed out. It is hoped to present results of direct measurements in subsequent papers.

Lottermoser and Maffia (*Ber. Ges.*, 1910, **43**, 3613) and Pauli and Matula (*Kolloid Z.*, 1917, **21**, 49) determined the distribution† of chlorine ions between the colloid ' micelle ' and the intermicellary liquid. The electrical conductivity of the sol is taken to consist of (*a*) that contributed by the micelle ions and the *free* oppositely charged electrolytic ions associated with them and (*b*) that of the electrolytes present in the intermicellary liquid. Maffia claimed that the ultrafiltrate gave the intermicellary liquid in an unchanged condition. " The results obtained by the ultrafilter could be

† Freundlich (*vide infra*) in explaining the equilibrium conditions points out the possibility of the surface changing with the concentration of electrolyte.

confirmed by those in which the intermicellary liquid was allowed to enter into equilibrium with the external liquid by dialysis " (Freundlich, *colloid and Capillary Chemistry, Eng. Ed.*, 1926, p. 372). This proposition has been tacitly assumed by later workers (McBain in connection with his work on soaps; Kruyt and Willigen, *Kolloid Z.*, *loc. cit.*). Pauli and Matula (*loc. cit.*) found from potential measurements that "the hydrogen-ion concentration proved to be not sensibly different from that in neutral solution, nor did it appreciably alter on coagulation by electrolytes. But chlorine-ion concentration suffers great changes on coagulation by electrolytes" (Freundlich, *loc. cit.* p. 374). Rabinovitsch (*Z. Phys. Chem.*, 1928, 133, 203) has recently investigated the changes in the concentration of oppositely charged ions on the addition of electrolytes.

Experimental.

Preparation of Sol: 10 C.c. of a saturated solution of ferric chloride were added drop by drop to 500 c.c. of boiling conductivity water with constant stirring and boiled for half an hour. The solution when cold was dialysed for a month and a half. It contained a trace of chloride. *The cataphoretic speeds* were measured by the method of moving boundary as improved by Mukherjee (*Proc. Roy. Soc.*, 1923, A **103**, 102). The boundary could be read satisfactorily when a blue glass was placed in front of the light. The upper liquid was prepared as given by S. N. Mukherjee (*Kolloid. Z.*, 1930, **52**, 68; see also Rai-Choudhuri and Bhattacharyya *loc. cit.*). *The silver-silver chloride electrodes* were prepared as given by Noyes and Ellis (*J. Amer. Chem. Soc.*, 1917, **39**, 2532). The *total chlorine* was determined by electrometric titration using a saturated solution of silver chloride for the reference electrode. A measured volume of the sol was dissolved in nitric acid, the iron precipitated, washed carefully, and the total filtrate collected. To a definite volume acidified with nitric acid, solid potassium nitrate was added so as to make its concentration 5% and titrated with a centinormal silver nitrate solution from a microburette. The titration was continued after the change in the sign of the E.M.F. The coagulating concentrations were determined as given by Chaudhury (*J. Cham. Soc.*, 1924, **125**, 794). The *ultrafiltration* was carried out by means of ultrafilters prepared from a high concentration

of collodion in an open pattern nickel plated ultrafilter. A pump was used for suction. The ultrafilters were carefully washed before use.

The ultrafiltrate was also used as upper liquid in cataphoretic measurements but did not give a satisfactory boundary condition. The potential gradient varied widely during the cataphoresis (*cf. J. Indian Chem. Soc.*, 1928, 5, 593). It is necessary* to draw attention to this observation for the method of moving boundaries gives entirely erroneous results unless the conditions for a satisfactory boundary as defined by Mukherjee are previously ascertained from a direct determination of the potential gradient across the boundary.

The measurement of hydrogen-ion concentrations in this sol present difficulties. Oxygen or glass electrodes may be used but it is doubtful whether they are accurate enough for our purpose. The hydrogen-ion concentrations of the clear liquid obtained by coagulating the sol with a small amount of solid potassium sulphate were determined. It is not known whether they give the correct hydrogen-ion concentration of the intermicellary fluid as stated by Pauli and Matula (*loc. cit.*).

Results.

TABLE II.

Sol A contains ·0422 mols of Fe_2O_3 per litre. A/2, A/4 have been obtained by diluting sol A to twice and four times its volume.

Sol.	Time of coagulation in minutes.	Coagulating concentrations (normal). KCl	K_2SO_4	$K_4Fe(CN_6)$
A	3	·23	·00069	·00 016
A/2	3	·23	·00039	·00013
A/2	6	·21	·00038	·000127
A/4	3	·23	·00028	·00007
A/4	12	·19	·00026	·000067

* *Cf.* Freundlich, *Kapillar Chemie*, 1930; Pauli, *Electrochemie der Kolloide*, 1929, p. 149; Kruyt and Willigen, *loc. cit.*, where the need for such direct determination s has been overlooked.

TABLE III.

Cataphoretic speeds $\times 10^5$.

Dilution.	Viscosity (taking the value of water as unity at the same temp.).	Speed. Direct.	Speed. Reverse.	Average speed (reduced to viscosity of water).
A	1·0396	49·52	50·35	51·43
		49·76	48·66	
		50·33	48·66	
A/2	1·0023	44·04	41·38	41·32
		39·58	41·77	
		41·13	39·57	
A/4	1·0011	49·23	50·28	49·79
A/6	1·0100	53·33	51·12	53·51
		52·6	54·93	
A/11	1·0002	58·21	58·59	58·41

TABLE IV.

Sol.	Specific conductivity in r.o.	Chlorine-ion conc. (normal) (20·5° to 22°).	Total chloride conc. (normal).	C_H (normal). 30°
A	·001039	·003166	·0104	·000369
A/2	·0005601	·00206	·0052*	·000316
A/4	·0003084	·001042	·0026*	·000098
A/6	·0002175	·0006982	·00173*	·0000619
A/11	·0001183	·0004656	·000945*	·0000271

* Calculated from that for Sol A.

TABLE V.

Cataphoretic speeds $\times 10^5$: Sol A/2.

Concentration of potassium chloride (normal).	Direct.	Reverse.	Average (reduced to viscosity of water).
0	44·04	41·38	
	39·58	41·77	41·24
	41·13	39·57	
0·001	41·74	43·26	43·11
	41·18	46·33	
0·01	41·37	40·51	41·55
	43·99	40·33	
0·05	42·14	39·39	40·89
	38·28	43·52	
0·067	38·95	39·59	40·83
	43·12	41·68	
0·1	40 54	37·93	39·76
	41·68	38·90	
0·125	40·39	35·91	39·47
	40·79	30·38 (coagulation of sol begins)	
0·125 (after coagulation)	32·58 (about 3 hrs. from starting of experiment). 27·47 (about 4 hrs. from starting of experiment).	33 94 24·54	29·63

TABLE VI.

Cataphoretic speeds $\times 10^5$: Sol A/11.

Concentration of potassium chloride (normal).	Direct.	Reverse.	Average (reduced to viscosity of water).
0	58·21	58·59	58·40
0·0002	51·18	55·11	54·73
	54·21	58·43	
0·001	51·95	52·97	51·82
	49·65	52·71	
0·01	39·91	39·25	39·51
	39·41	39·50	
0·02	37·49	39·96	38·56
	36·17	40·65	
0·083	33·20*	32·46*	32·83
During coagulation. 0·1	37·03*	26·57 (Coagulates)	—
After coagulation. 0·1	19·85	Particles settle down and boundary gets disturbed.	19·65

* Boundary becomes convex.

TABLE VII. Sol B.

Cataphoretic speeds $\times 10^5$ with different upper liquids including the ultrafiltrate.

Contains 0·0143 mols. of Fe_2O_3 per litre: $p_H = 2·004$.

Upper liquid.	Pot. grad. before cataphoresis.	Pot. grad. after cataphoresis.	Direct movement.	Pot. grad. before cataphoresis.	Pot. grad. after cataphoresis.	Reverse movement.	Average (reduced to viscosity of water).
Equiconducting HCl	1·110	1·138	50·43	1·174	1·176	47·26	
	1·112	1·108	50·96	1·123	1·100	49·96	49·58
	1·132	1·123	50·25	1·141	1·127	48·65	
Ultrafiltrate	1·054	1·009	38·77	1·017	1·075	54·13	46·33
	1·035	0·9895	40·62	1·022	1·080	51·81	
	Speed for residual sol after ultrafiltration.						
Usual upper liquid	1·016	1·046	43·10	1·091	1·034	41·84	42·14
	1·059	1·047	41·14	1·096	1·047	42·51	

TABLE VIII.

Sol B — Analysis.

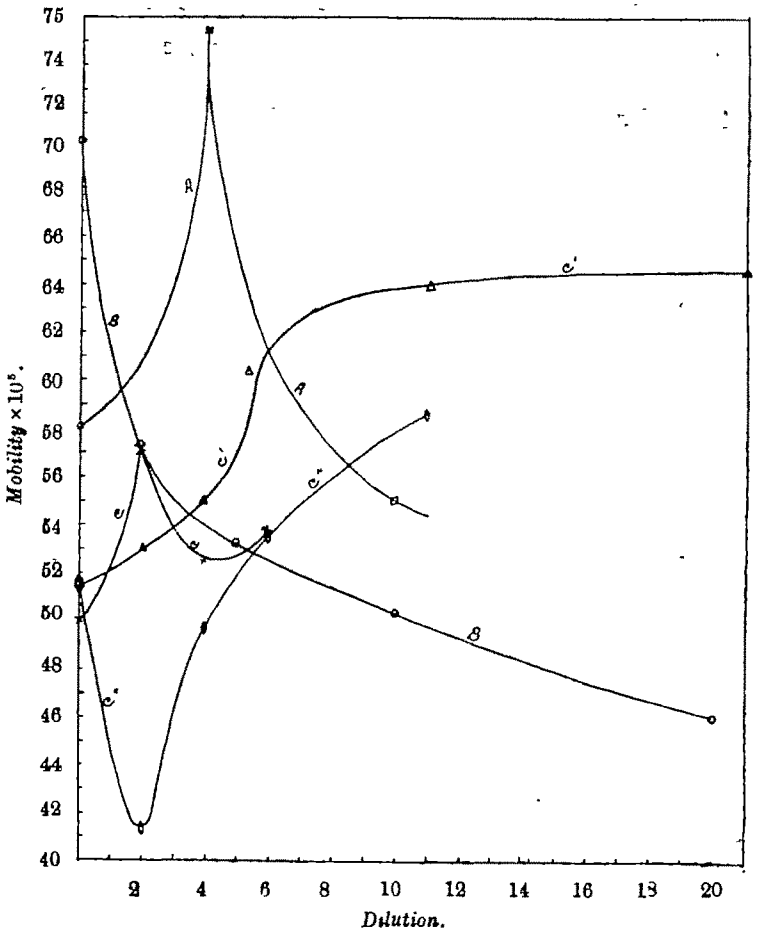
	Specific conductivity (r.o.).	Chlorine-ion concentration (normal).	Total chloride concentration (normal).
Sol B	·002563	·006985	·008568
Supernatant liq. after coagulation by K_2SO_4	—	·007408	·00777
Ultrafiltrate	·002245*	·005761	·005932
	·002165		
Residual sol after ultrafiltration	·002480	·007408	·01554

* Specific conductivity of ·005761 *N*-hydrochloric acid.

Discussion.

(*a*) *Changes brought about by dilution.*—In agreement with previous observations the coagulating concentration (Table II) of the divalent and trivalent oppositely charged ions decreases on dilution; while that for potassium chloride remains constant so long as the time of coagulation remains the same. But if the time is made proportional to the dilution (as suggested by Usher, *Trans. Faraday Soc.*, 1926, **21**, 406) the electrolyte also shows a sensitisation, indicating a change in the condition of the particles.

FIG. 1.



Curves A, B, C *and* C′ *are as in S. N. Mukherjee, Kolloid Z*, 1930, **52**, 68; *Curve* C″ *from the data in Table* III *of this paper.*

In Fig. 1 are collected the changes in the cataphoretic speeds produced on dilution (*vide Kolloid Z.*, 1930, **52**, 68). Dilution by changing the environment brings into operation a large number of factors. The hydrogen-ion concentration (as observed after coagulation by solid K_2SO_4, S. N. Mukherjee, *loc. cit.*) decreases on dilution. The concentration of the free chlorine ions and the total chlorine have been determined directly [1] (Table IV). Assuming [2] that the concentration of the free ions (hydrogen [3] and chlorine) given

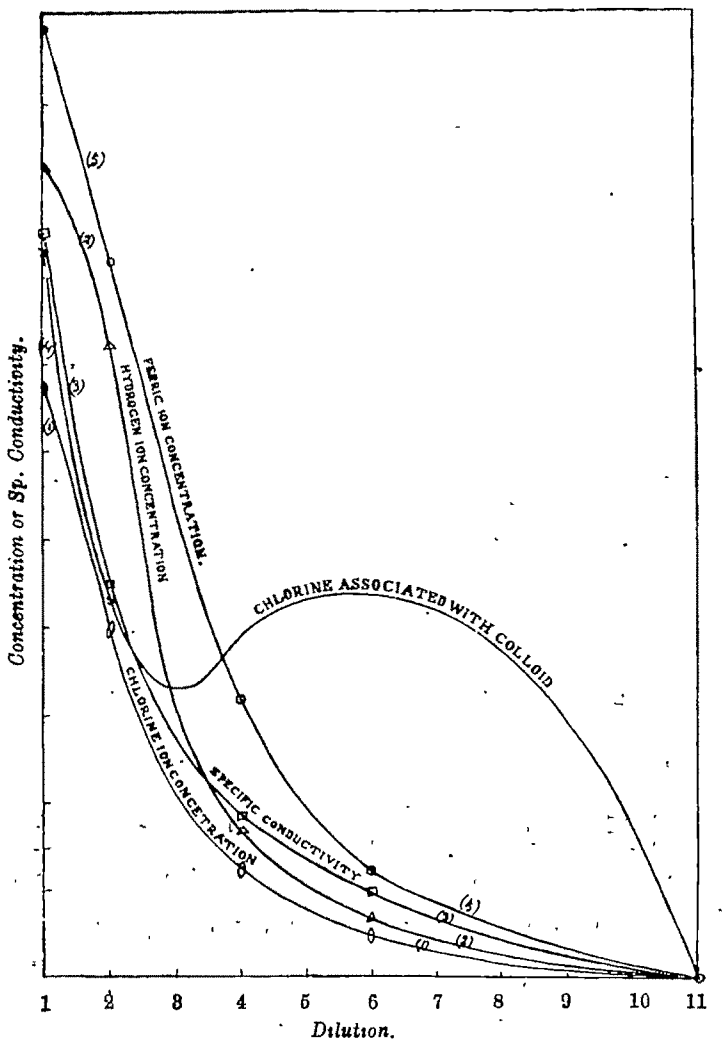
[1] The concentrations of the iron and hydrogen ions are subject to uncertainty as they have been indirectly determined. It is proposed to eliminate this uncertainty in a subsequent paper.

[2] The validity of this assumption is the subject matter of a separate investigation (*vide* Introduction).

[3] *Cf.* Pauli and Matula, *loc. cit.*

in these tables are those of the intermicellary liquid, the concentration of ferric ions present in it, is given by the difference between them. Deducting from the observed specific conductivity of the sol the conductivity contributed by these three ions (Kohlrausch and Holborn, *Das Leitvermögen der Elektrolyte*, 1916), we obtain

FIG. 2.



In the ordinate different units are chosen for convenience of plotting :

Associated chlorine	—1 div. = ·0021;	origin refers to	·0058*N*.
Chlorine-ion conc.	—1 div. = ·0004	,, ,,	·0035*N*.
H^+-ion conc.	—1 div. = ·00004	,, ,,	·00008*N*.
Sp. conductivity	—1 div. = ·0001	,, ,,	000118 r.o.
$\frac{1}{3}Fe^{+++}$-ion conc.	—1 div. = ·00016	,, ,,	·00043*N*.

the conductivity contributed by the charged micelle and its associated ions. The specific conductivity of the sol also steadily decreases with dilution. The concentration of the free chlorine and hydrogen ions show a remarkable parallelism with the change in the specific conductivity of the sol on dilution (Fig. 2, curves 1, 2, and 3 respectively).

The complicated variation in the cataphoretic speed on dilution is in contrast to the above. The cataphoretic speed of the particles has little effect on the specific conductivity as such, or *vice versa*. In curve 4, Fig. 2 the amount of chlorine per litre '*associated*' with the colloidal particles has been plotted against the dilution. This quantity has been calculated on the assumption that the free chlorine-ion concentration gives the chlorine present in the intermicellary liquid. The associated chlorine would then be equal to the excess of the total chlorine (estimated per litre of the original sol) over the free chlorine-ion concentration of each dilution multiplied by the dilution. The associated chlorine does not show the regular variation observed with the other quantities. The changes in the cataphoretic speed cannot also be correlated with it. Fig. 1 shows that considerations of activity coefficients, and ionic strengths are insufficient (Pauli, *loc. cit.*, p. 172; Pennycuick, *J. Chem. Soc.* 1930, p. 1447, and earlier publications).

(b) *Changes produced by Ultrafiltration.*

From Table VIII it appears that the chlorine-ion concentration of the ultrafiltrate is considerably less than that of the free chlorine ions in the sol. Moreover the conductivity of the ultrafiltrate is less than what it would be if the chlorine was present solely as hydrogen chloride. A trace of ferric ions might be assumed to be present.[4] The possible presence of very fine (amicrons) colloidal particles of iron is also not excluded. The presence of cations other than hydrogen ions is also shown by the excess of the total chlorine over the free chlorine ions in the ultrafiltrate. The liquid obtained after coagulation of the colloid with potassium sulphate has a much higher concentration of 'free' chlorine ions than that of the ultrafiltrate or of the original sol. The residual sol after ultrafiltration has exactly the same chlorine-ion concentration as that of the liquid obtained by coagulation which is possibly a chance coincidence. The total chlorine in the residual sol is greater than that of the original sol but that of the supernatant liquid is less than both these quantities. *Ultrafiltration clearly produces a*

[4] The thiocyanate test gave a negative result.

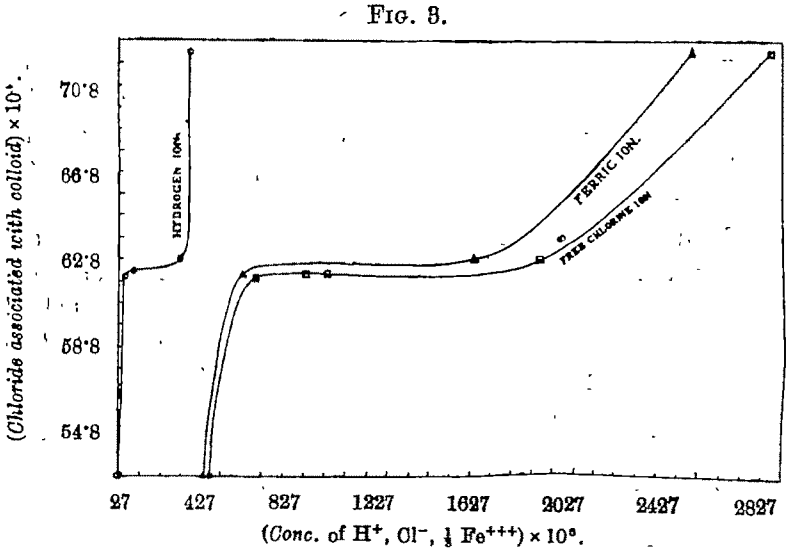
change in the composition of the intermicellary fluid. Less of the free chlorine ions pass out and their concentration increases in the residual sol. The smaller conductivity of the latter shows that it is poorer in hydrogen ions.

(c) *The Ultrafiltrate as the Upper Liquid in Cataphoretic Measurements.*

From Table VII *it will also be seen that the ultrafiltrate is not satisfactory as the upper liquid.* This is shown by the marked difference between the cataphoretic speeds in the upward and downward movements. The constancy between the potential gradient as also the agreement between the upward and downward speeds with the usual upper liquid evidently satisfies the theoretical requirements for a uniform ionic environment. Since this liquid is obtained by adding a trace of concentrated ferric chloride to the liquid obtained after coagulation it seems likely that the latter has a higher hydrogen-ion concentration than that of the intermicellary fluid determined as above. At any rate, these results show (*a*) that the ultrafiltrate has not the same composition as the intermicellary fluid (*b*) the liquid obtained by coagulation has a different hydrogen-ion concentration than that of the intermicellary fluid and (*c*) the use of the ultrafiltrate as an upper liquid in cataphoretic measurements (Kruyt and Willigen *loc. cit.*) is not justified and gives erroneous results in the former instance.

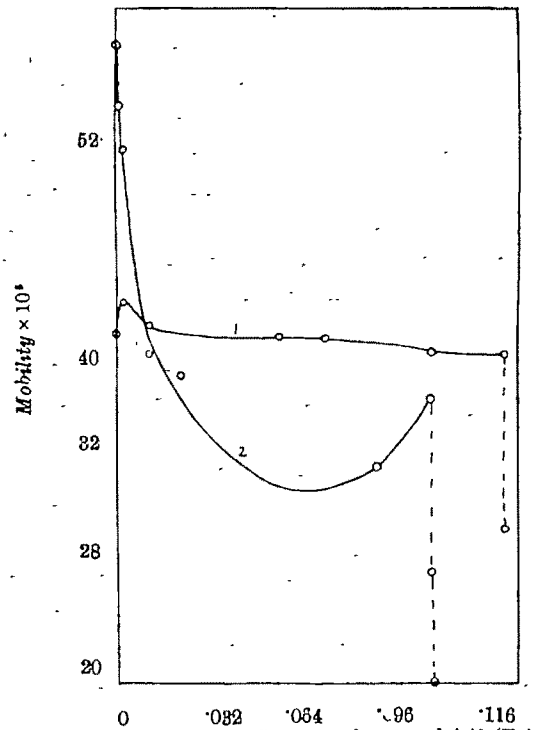
(d) *The Cataphoretic speed in relation to the Composition of the Intermicellary liquid.*

FIG. 3.



In Fig. 3 have been plotted the concentrations of the free hydrogen, iron and chlorine ions against that of the chlorine ions associated with the colloid. It appears that over a considerable range beginning with the first dilution, the associated chlorine remains fairly constant. On either side of this range the associated chlorine decreases with the concentration of the free ions. Assuming that the number of particles per unit volume is proportional to the dilution, curve (4) in Fig. 2 indicates a rapid increase of the number of free chlorine ions in the intermicellary liquid and a corresponding diminution in the number associated with the colloid micelles. In the middle portion of the curve the reverse process appears to take place to a small extent. This is probably associated with the observed increase in the cataphoretic speed after the first dilution. On comparing the manner of variation of the cataphoretic speed (Fig. 1) with the curves in Fig. 3, it is possible to draw a picture as to how the speed depends on the composition of the electrolyte. The number of ferric ions per unit surface of the colloidal particle may be assumed to be determined by the concentration of ferric ions (or rather of hydrogen ions which determine their stability) in the intermicellary liquid. At the first dilution there is a rapid fall in the concentration of these ions, as also in the number of positive electronic charges in the form of ferric ions per unit surface. Possibly each of the ferric ions in the surface hydrolyses and forms ions of the basic residue with two or one free electronic charges [*e.g.*, $Fe(OH)Cl_2$, $Fe(OH)Cl_2$]. The fall in the amount of associated chlorine at the first dilution is indicative of such a change. For the next stages of dilution, the number and type of such complexes do not seem to vary widely with further changes in the concentration of these ions. Curve 4 (Fig. 2) confirms this conclusion. On further dilution, progressive hydrolysis takes place resulting in the removal of chlorine ions from the interface. The increase in the speed at greater dilutions together with the small variation of the associated chlorine for the next two dilutions indicate that with further decrease in the concentration of chlorine ions in the intermicellary liquids, an increasing fraction of the associated chlorine passes from the solid side of the interface to the liquid side.

FIG. 4.



Concentration of KCl in normality ; Curve 1 refers to sol A/2 (Table V); Curve 2 refers to sol A/11 (Table VI).

FIG. 5.

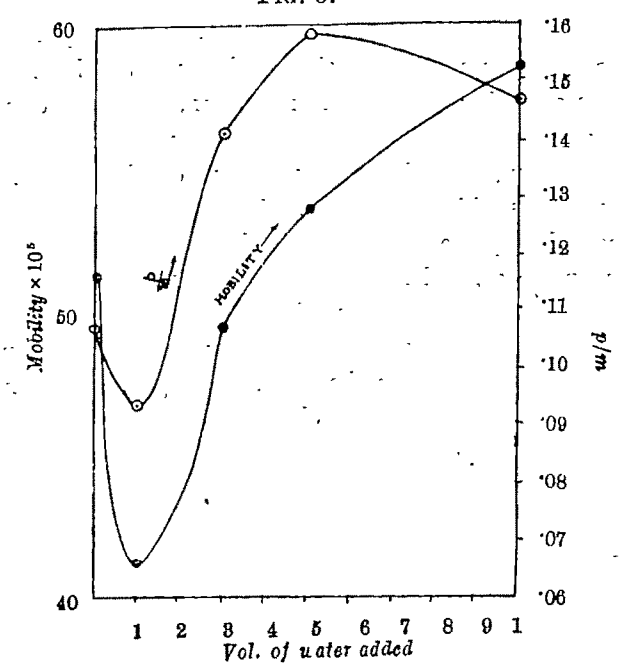


Fig. 4 shows that no direct relationship can justifiably be assumed to exist between the cataphoretic speed and ionic strength (Pauli, Pennycuick, *loc. cit.*) on the basis of the Debye-Hückel theory. For though the added electrolyte is present in concentration and is the same in both, the forms of the two curves are widely different. Also the valencies of the colloidal particles are unknown and the sol is a polydisperse one. It is also to be observed that no simple relationship exists between the initial speed and the coagulating concentration. In fact the sol with higher initial speed has a lower speed as also a lower coagulating concentration at the coagulation point. The curves further show a drop in the cataphoretic speed after coagulation with progress of time. These observations are in agreement with the previous observations with arsenious sulphide sol in this laboratory. The small but definite difference in the cataphoretic speed at the coagulation point and the shapes of the two curves show that the supposed existence of a critical coagulating potential is not borne out by facts.

The Cataphoretic Speed and the Surface Density of the Electrical charge.

The density of the charge is the one electrical factor which admits of a direct relationship with the fixation of ions on the solid side of the interface (see *Trans. Faraday, Soc., loc. cit.; Phil. Mag., loc. cit.*). The assumption that the density is proportional to the cataphoretic speed requires theoretical and experimental justification. It can be experimentally tested as follows. We shall first define what we have called the 'equivalent concentration' of the colloidal particles. It is equal to the number of colloidal particles per litre multiplied by the *average* number of electronic charges per particle expressed in terms of the customary unit in electrochemistry (96540 coulombs). It can be calculated if the cataphoretic speed, the mobility of the free ions associated with the colloidal particle and the conductivity of the colloidal particles are known. If Q is the number of electrochemical equivalents (of the micelle ions) per litre and δ is the sum of the equivalent conductivities of the associated free chlorine ion and of the micelle ions then we have:

$$P = Q.\delta \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where P is thousand times the specific conductivity of the colloidal

particles as distinct from that of the intermicellary liquid. The equivalent conductivity of the charged colloidal particle (micelle ion) is given by the cataphoretic speed multiplied by the electrochemical unit of electricity. On the assumption that the cataphoretic speed U (which is independent of the size) is proportional to the density of the electric charge, we have $U=K.n$ ..... (2) where n is the number of electronic charges per unit surface. The actual number per particle is proportional to the surface. We then have $Q=n.N.S$ .....(3) where N is the number of colloidal particles per litre and S is equal to the *arithmetic mean* surface of the particles. Further $\delta=(U+V)F$ ... (4) where V is the speed of the associated *free* anions assumed to be of one sort only, whence it follows that $P=n.\ N.\ S.\ (U+V)F=\frac{U}{K}.\ N.\ S.\ (U+V)F$ ... (5). Relationship (5) can be tested for different dilutions assuming further as is usual that the number of particles per unit volume is proportional to the dilution.

The product $\delta.Q$ can be obtained from the following relation

$$R=\alpha x+\beta y+\gamma z+\delta.Q \quad \ldots \quad (6)$$

where R is thousand times the specific conductivity of the sol, α, β, γ are respectively the equivalent conductivies of chlorine, hydrogen and ferric ions and x, y, z are respectively the number of gram equivalents of these ions per litre of the sol.

From the equivalent concentration of the colloidal particle, m, calculated from equation (2) and the number of gram mole, p of ferric oxide per litre of the sol, it is possible to calculate the number of molecules of ferric oxide, m/p, with which one electronic unit of charge is associated (*vide* column 12 of Table IX). It is interesting to note that the reciprocals of the sequantities (excepting the last values) fairly represent the trend of the curve (Fig. 5) showing the variation in the cataphoretic speed with dilution. It should be emphasised that some of the values have been obtained in an indirect manner and that several assumptions have been made which though often accepted as true, require adequate justification by further experiments. The error in calculating $\delta.Q$ increases as the dilution increases. Also the silver-silver chloride electrode is not completely satisfactory for these solutions.

In Table IX are collected the data for different dilutions of the sol as follows:—Column 1 gives the dilutions of the sol; 2, the

cataphoretic speeds (u) at 35° in cm./sec. per volt/cm. $\times 10^5$; 3, the value for $u' = uF$, in reciprocal ohms at room temperature (20°·5); column 4 gives P, the specific conductivity of the sol at 20°·5; columns 5, 6, 7, 8 give the equivalent concentrations per litre respectively of free chlorine ions (x), the total chloride, hydrogen ions (y) and iron ions (z); column 9 gives the value for the product $\delta.Q$, where δ is the sum of the equivalent conductivities of chlorine ions a and u', that of the micelle ion extrapolated for 20°·5 assuming the speed to be inversely proportional to the viscosity. In columns 10 and 11 are given the equivalent concentrations of colloidal particles calculated as explained above and the number of gm. moles of ferric oxide per litre; m/p, the number of molecules of ferric oxide with which one electronic charge is associated, is given in the column 12.

The concentrations of the ions in the following table have been calculated assuming complete dissociation. The activity coefficients can be obtained from the equivalent conductivity by a method of approximation and the values if corrected in this manner give better agreement.

TABLE IX.

1	2	3	4	5	6	7	8	9	10	11	12
Pure sol	51·43	35·16	·001089	·003166N	·0104N Estimated.	·000869N	·00279N	·0005225	·0050N	·0422M	8·4
1 :1	41·32	28·25	·000560	·00206N	·0052N Calculated.	·000316N	·001744N	·0002040	·0021N	·0211M	10·0
1 :3	49·79	34·03	·000308	·001042N	·0026N Calculated.	·000098N	·0009439N	0001446	·0014N	·0105M	7·5
1 :5	53·51	36·58	·000217	·0006982N	·00178N Calculated.	·0000619N	·0006368N	·0001087	·0010N	·00703M	7·0
1 :10	58·41	39·93	·000118	·0004656N	·000945N Calculated.	·0000271N	·0004385N	·0000495	·00045N	·00383M	8·5

In conclusion it is necessary to emphasise that some of the conclusions of the present paper are of a tentative character.

THE UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY.
PHYSICAL CHEMISTRY LABORATORY,
CALCUTTA.

Received January 8, 1931.

Benzene- and Naphthalene-azo-*o*-coumaric Acids.

By Duhkhaharan Chakravarti.

Borsche (*Ber.*, 1904, **37**, 846) observed that an alkaline solution of coumarin, like a phenol, forms an azo-compound when coupled with diazotised aniline. To obtain definite information about the question as to whether hydroxyazo-compounds are azophenols or quinone-phenylhydrazones, Mitchell (*J. Chem. Soc.*, 1905, **87**, 1229) and Hewitt and Mitchell (*J. Chem. Soc.*, 1906, **89**, 13, 17) prepared a series of azo-compounds by coupling diazo-salts with coumarin in alkaline solution.* They failed to isolate benzeneazocoumaric acid due to the ready formation of the lactonic ring. While investigating the effect of the lactonic group on the colour of an azo-dye, it has been thought advisable for a comparative study to break up the lactones and isolate the free hydroxy acids, and accordingly the corresponding azo-*o*-coumaric acids, the geometrical isomers of the azo-coumarinic acids, have been prepared.

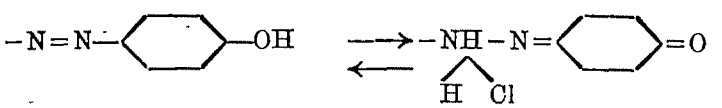
It is interesting to find that when an alkaline (about 1%) solution of the benzene- and naphthalene-azocoumarins is boiled for some time with a small quantity of mercuric oxide (red or yellow), the sodium salts of the azocoumarinic acids undergo geometrical inversion quantitatively to the salts of the azo-*o*-coumaric acids. In this respect the azo-grouping behaves like a negative substituent (*cf.* Sen and Chakravarti, *J. Indian Chem. Soc.*, 1930, **7**, 247). The action of mercuric oxide seems to be purely catalytic as it remains unchanged at the end of the operation.

That the acids, thus isolated, are not azo-coumarinic acids but azo-*o*-coumaric acids, is conclusively proved by the direct synthesis of some of them from *o*-coumaric acid itself. Thus benzene-azo-*o*-coumaric acid (Borsche and Streitberger, *Ber.*, 1904, **37**, 4116), *p*-nitrobenzeneazo-*o*-coumaric acid, diphenylbisazodi-*o*-coumaric acid, naphthalene-α-azo-*o*-coumaric acid have also been directly synthesised from *o*-coumaric acid by coupling it in an alkaline solution with diazotised aniline, *p*-nitraniline, benzidine and α-naphthylamine respectively.

* When the 6-position in the coumarin molecule is free, coupling takes place in the 6-position, as is proved by the reduction of benzeneazocoumarin to 6-amino-coumarin.

These azocoumaric acids are beautifully crystalline substances, readily soluble in alcohol and other solvents unlike the corresponding azocoumarins, which are very difficultly soluble in the ordinary solvents. They dissolve freely in sodium bicarbonate solution with effervescence. The colour of these dyes varies from yellow to red and even the naphthalene-azocoumarins (α and β) are yellow to brown, while the corresponding naphthalene-azo-*o*-coumaric acids have a green tinge.

A remarkable phenomenon which has been observed in the case of all these azo-*o*-coumaric acids is that they undergo in the solid state a marked change of colour when in contact with hydrochloric acid, the colour changing on dilution of the acid. Thus in the presence of concentrated hydrochloric acid, the yellow diphenylbisazodi-*o*-coumaric acid becomes violet, the naphthalene-α-azo-*o*-coumaric acid (greenish-yellow) becomes deep green, the original colour of the compounds being recovered on dilution (*vide* Table I). This change of colour seems to give a direct experimental evidence to the hypothesis advanced by Hewitt and his collaborators (*J. Chem. Soc.*, 1901, **79**, 160; 1905, **87**, 225) that the *p*-hydroxyazocompounds are true azophenols and not quinonephenylhydrazones and that in the presence of strong mineral acids they may possibly possess a quinonoid constitution in the form of salts.



It is noteworthy however, that the azo-derivatives of the 4-alkylcoumarins do not generally form *o*-coumaric acids by this method probably due to the unstability of the β-alkyl-*o*-coumaric acids (Fries and Klostermann, *Annalen*, 1908, **362**, 1); only in the case of benzeneazo-4:6-dimethylcoumarin the corresponding *o*-coumaric acid has been isolated in very poor yield. This acid also seems to be very unstable readily changing back into the coumarin.

Experimental.

Benzeneazo-o-coumaric acid.—A solution of benzeneazocoumarin (Mitchell, *J. Chem. Soc.*, 1905, **87**, 1229) (3 g.) in caustic potash (4 g. in 25 c.c. water) is diluted with water (500 c.c.) and boiled for about an hour with powdered yellow mercuric oxide (3 g.). The

cold solution is filtered from the mercuric oxide and acidified with hydrochloric acid. The reddish-yellow precipitate, thus obtained, is thoroughly washed with water and dissolved in ammonia. The ammoniacal solution is filtered and acidified with hydrochloric acid and the precipitate filtered, dried and crystallised from dilute alcohol in fine yellow needles, decomposing at 205°. (Found: N, 10·5. $C_{15}H_{12}O_3N_2$ requires N, 10·44 per cent.).

The identical benzeneazo-*o*-coumaric acid decomposing at 205° has also been synthesised from *o*-coumaric acid by diazotising aniline (1·1 g.) and coupling it with an alkaline solution of *o*-coumaric acid (2 g.). The precipitate, obtained after acidifying the alkaline solution, is dissolved in ammonia and the filtered solution is acidified with hydrochloric acid and the precipitate crystallised from dilute alcohol. (Found: N, 10·53. $C_{15}H_{12}O_3N_2$ requires N, 10·44 per cent.).

Reduction of Benzeneazocoumarin.—Benzeneazocoumarin is reduced with stannous chloride and hydrochloric acid. The solution is made alkaline with caustic soda and the voluminous precipitate is extracted with boiling water, when 6-aminocoumarin melting at 167° crystallises in beautiful straw-yellow needles.

o-*Nitrobenzeneazo-o-coumaric acid* is prepared from *o*-nitrobenzeneazocoumarin (Mitchell, *loc. cit.*). The method of isolation and the purification of the compound is the same as in the previous case; crystallised from dilute alcohol, it decomposes at 223°. It is a brownish-yellow substance. (Found: N, 13·7. $C_{15}H_{11}O_5N_3$ requires N, 13·4 per cent.).

m-*Nitrobenzeneazo-o-coumaric acid* is obtained from *m*-nitrobenzeneazocoumarin (Mitchell, *loc. cit.*). The compound is isolated as usual. It is crystallised from dilute alcohol in microcrystalline deep yellow powder decomposing at 213°. (Found: N, 13·33. $C_{15}H_{11}O_5N_3$ requires N, 13·4 per cent.).

p-*Nitrobenzeneazo-o-coumaric acid* prepared from *p*-nitrobenzeneazocoumarin (Mitchell, *loc. cit.*), is crystallised from dilute alcohol. It is a reddish-yellow substance decomposing at 236°. (Found: N, 13·62. $C_{15}H_{11}O_5N_3$ requires N, 13·4 per cent.).

The identical compound has been prepared directly from *o*-coumaric acid by coupling diazotised *p*-nitraniline with an alkaline solution of *o*-coumaric acid. The precipitate, obtained after acidifying the alkaline solution is dissolved in ammonia and is reprecipitated with acid. The precipitate is washed with water and crystallised

from dilute alcohol; decomp. 236°. (Found: N, 13·28. $C_{15}H_{11}O_5N_3$ requires N, 13·4 per cent.).

Diphenylbisazodicoumarin.—Tetrazotised benzidine solution is added to an alkaline solution of coumarin and the mixture kept overnight. The solution is acidified with hydrochloric acid and the voluminous precipitate is filtered and thoroughly washed with boiling water. The dried residue crystallises in beautiful needles (not melting up to 280°) from a large volume of boiling nitrobenzene. It dissolves in caustic alkalis with a red solution and in concentrated sulphuric acid with a violet solution. It is insoluble in the ordinary organic solvents. (Found: N, 11·56. $C_{30}H_{18}O_4N_4$ requires N, 11·24 per cent.).

Diphenylbisazodi-o-coumaric acid is obtained from diphenylbisazodicoumarin as in the previous cases. The dried crude product is dissolved in pyridine and poured into toluene when a yellow precipitate is obtained which is filtered and washed with benzene. It is a micro-crystalline yellow substance decomposing at 315°. (Found: N, 10·66. $C_{30}H_{22}O_6N_4$ requires N, 10·5 per cent.).

The identical diphenylbisazodi-*o*-coumaric acid, decomposing at 315°, has also been obtained directly from *o*-coumaric acid by coupling tetrazotised benzidine solution with an alkaline solution of *o*-coumaric acid. It is finally dissolved in pyridine and poured into toluene and the yellow precipitate collected. (Found: N, 10·72. $C_{30}H_{22}O_6N_4$ requires N, 10·5 per cent.).

Naphthalene-α-azocoumarin.—It is prepared by adding diazotised α-naphthylamine solution to an alkaline solution of coumarin. The filtered solution is then acidified with hydrochloric acid and the red precipitate is filtered and thoroughly washed with boiling water. The precipitate is then crystallised from toluene in stout brown prisms or needles melting at 217°. It dissolves in caustic alkalis forming a deep-red solution and in concentrated sulphuric acid with a blue solution. (Found: N, 9·6. $C_{19}H_{12}O_2N_2$ requires N, 9·3 per cent.).

Naphthalene-α-azo-o-coumaric acid is prepared from naphthalene-α-azocoumarin and is crystallised from dilute alcohol in shining greenish-yellow needles decomposing at 198-200°. (Found: N, 9·1. $C_{19}H_{14}O_3N_2$ requires N, 8·8 per cent.).

The identical naphthalene-α-azo-*o*-coumaric acid decomposing at 198°-200° has also been obtained directly by coupling diazotised α-naphthylamine with an alkaline solution of *o*-coumaric acid. It

is finally crystallised from dilute alcohol in shining yellow needles. (Found: N, 9·05. $C_{19}H_{14}O_3N_2$ requires N, 8·8 per cent.).

Naphthalene-β-azocoumarin is prepared by coupling diazotised β-naphthylamine with an alkaline solution of coumarin. The red solution, after keeping overnight, is acidified with hydrochloric acid and the precipitate filtered and thoroughly washed with boiling water. The substance crystallises from pyridine in beautiful needles. It also crystallises from toluene, in which it is not so much soluble. It is a yellow substance melting at 271°; it dissolves in caustic alkalis (an orange solution) and in concentrated sulphuric acid (a deep-red solution). (Found: N, 9. $C_{19}H_{12}O_2N_2$ requires N, 9·3 per cent.).

Naphthalene-β-azo-o-coumaric acid is prepared from naphthalene-β-azocoumarin. It crystallises from dilute alcohol as a microcrystalline pale yellow substance, decomposing at 210°. (Found: N, 9·12. $C_{19}H_{14}O_3N_2$ requires N, 8·8 per cent.).

Benzeneazo-β:5-dimethyl-o-coumaric acid is prepared from benzeneazo-4:6-dimethylcoumarin. The procedure of dissolving in ammonia and precipitating with acetic acid is repeated several times, as the compound seems to be very unstable and forms a turbid solution in ammonia which is very difficult to filter. It is then dissolved in alcohol and poured into water and the solid, that separates, is collected and extracted with ether. It decomposes at 186° (yield 20%). (Found: N, 9·12. $C_{17}H_{16}O_3N_2$ requires N, 9·46 per cent.).

TABLE I.

Colour of Azo-o-coumaric Acids.

Name.	Colour in the solid state.	Colour with alkalis.	Colour with conc. sulphuric acid.	Colour with conc. hydrochloric acid.
Benzeneazo-o-coumaric acid	Yellow	Orange	Red	Red
o-Nitrobenzeneazo-o-coumaric acid	Brownish-yellow	Deep-red	Deep-red	Reddish-brown
m-Nitrobenzeneazo-o-coumaric acid	Deep-yellow	,,	Red	Brick-red
p-Nitrobenzeneazo-o-coumaric acid	Reddish-yellow	Scarlet-red	,,	Reddish-brown
Diphenylbisazodi-o-coumaric acid	Yellow	Deep-red	Deep-violet	Violet
Naphthalene-α-azo-o-coumaric acid	Greenish-yellow	Port wine-red	Bluish-violet	Deep-green
Naphthalene-β-azo-o-coumaric acid	Pale-yellow	Light-red	Deep-violet	Red

The author wishes to express his grateful thanks to Prof. R. N. Sen for his kind interest and suggestions.

CHEMICAL LABORATORY.
PRESIDENCY COLLEGE, CALCUTTA.

Received May 8, 1931.

The Chemistry of Jute-lignin. Part I. A Comparative Study of Different Methods of Isolation.

By Pulin Behari Sarkar.

The fundamental difference in the composition of jute and cotton, is that the ultimate lengths of single cells of jute are much less than that of cotton (about 0·6 mm. for jute and 30—40 mm. for cotton) and that these single cells are joined together by a gummy matter in the case of jute, as a result of which the fibre appears much longer. The percentage of this incrusting material is pretty high, being about 25 per cent. In fact, cotton is 98 per cent. pure cellulose, whereas jute contains only 74 per cent. The incrusting matter on the cell-walls of jute fibre consists mainly of lignin, hemi-celluloses, uronic acids and pectin. These constituents obviously modify the physical and chemical properties of the fibre to a very great extent. But the function played by each individually is not yet definitely known; neither the way in which these substances occur in the fibre, nor the relationship, if any, that exists amongst them, has been established. Thus, there exists a good deal of controversy as to the nature of existence of lignin in lingo-celluloses; some hold it to be a case of physical adsorption whilst others are of opinion that the two are chemically combined. In order to study the effects of these constituents on the properties of cellulose in the case of jute, each individual must be studied separately. Lignin is by far the most important constituent of the cell-wall, forming as it does, as much as 15 per cent. It was therefore thought advisable to study first of all this important member.

The simple ligno-cellulose typified by the annual jute forms a much more promising starting point for the study of lignin than the various woods. The low ash-content also indicates the suitability of the jute-lignin for scientific investigations.

While attempting to study a natural product, specially when it exists in conjunction with several others, the most important point that should always be borne in mind, is that it must be isolated in the least drastic way, using the mildest reagents, so that it may not

suffer any appreciable change during isolation. If this is ignored, we get not the genuine substance, but only a decomposition product, the study of which may not serve any useful purpose. It was therefore necessary to make first of all, a comparative study of the different methods of isolation of lignin, with the most recent modifications, in order to select the best one, most suitable for jute.

As the composition of jute fibre varies from sample to sample so far as these constituents are concerned, the same sample was used throughout the investigation. The middle portion of the jute was taken rejecting about 4 inches from below and one foot from above. The fibres were mechanically separated as far as possible, cut into small pieces, and the adhering foreign matter was removed first by simply washing with water several times and then by treating with neutral soap using distilled water all the while. The method of removing resin and fat by boiling with 0·5 per cent. caustic soda was rejected as it was found that a small amount of lignin was removed thereby.

In the case of timbers, Mehta (*Biochem. J.*, 1925, **19**, 958) found lignin partly in the free state (from 0·32 to 22·8 per cent.) in different timbers, directly extractible by alcohol, and partly in combination with cellulose hydrolysable with alkali. Accordingly jute was extracted with alcohol (95 per cent.) in a Soxhlet for about six hours, the residue obtained from the extract amounted to only 0·87 per cent. which failed to give any test for lignin. Jute was also extracted with acetone-alcohol mixture (2 : 1) which is an excellent solvent for 'free' alkali lignin, but no trace of lignin could be found in the residue obtained from the extract.

Resin and fat were removed by extracting the fairly dried jute with a mixture of alcohol-benzene (1 : 1); only one extraction for six hours was found to be quite sufficient. Jute thus treated was used in this investigation.

The moisture content of the fibre varied within wide limits during the year—thus in August (rainy season) the percentage of moisture was 15·75, in December (winter) it was 12·04 and in March (summer) it has been found to be 8·4 only. The usual constants were therefore calculated always on dry jute. The results of analysis of the jute used for the study of lignin are given below:

α-Cellulose ...	67·0 per cent.	Moisture ...	8·4 to 15·75 per cent.
Furfural ...	9·64 per cent	Ash ...	0·51 per cent.
Resin and fat...	0·91 per cent.	Uronic acids...	8·0 per cent.

Distribution of Lignin along the Fibre.—The lower part of the fibre is more deeply coloured than the upper one. It was thought that the higher percentage of lignin was the cause. The jute was therefore cut into three equal portions, purified in the usual way and lignin was estimated by hydrochloric acid method (*Ber.*, 1913, **46**, 2401) in each portion. The percentages were 15·38, 15·40, 15·41 showing that lignin was homogeneously distributed along the fibre. This fact lends some support to the theory that in lignocelluloses lignin is chemically combined with cellulose.

The ash has been subsequently found to accompany tenaciously the lignin isolated by acid hydrolysis; it was therefore qualitatively analysed and the following metals have been detected in the same, *viz*,. Mg, Ca, Fe, and Al; silica has also been found. The presence of some of these at least, *e.g.*, Ca and Mg might be attributed to the pectin present in jute. It was therefore attempted to remove the pectin first without isolating lignin. 0·5 Per cent ammoniumoxalate is a very good solvent for pectin and it has been shown by Chowdhury and Mitra (in a paper to be shortly published) from this laboratory that pectin can be quantitatively removed by two extractions with ammonium oxalate from jute completely delignified by chlorine peroxide. But in the case of raw jute, only a small amount of pectin could thus be extracted by the present investigator even by ten repeated extractions. It appears quite probable that lignin serve as a protective coating—which is impervious to ammonium oxalate. A pectin-lignin combination does not seem to be probable inasmuch as lignin alone and no pectin has been found to be present in various timbers (Ritter, *Ind. Eng. Chem.*, 1925, **17**, 1194).

As pectin has been found to be readily hydrolysable by acids, its presence cannot interfere with the estimation of lignin by the acid process. The metallic radicals in that case give salts soluble in water. So lignin was estimated without removing pectin beforehand. Hemi-celluloses are also very readily hydrolysed to water-soluble sugars on boiling with dilute acids and so it was unnecessary to remove them previously by 5 per cent. caustic soda in the cold.

Extractions with various other neutral solvents for the isolation of free lignin was found to be quite useless. The lingocellulose had to be hydrolysed either by acids or alkalis in order to obtain the lignin. There are at present altogether five different methods for the estimation of lignin, *viz.*, (*a*) by caustic soda under pressure, (*b*) by 42 per cent. hydrochloric acid at ordinary temperature, (*c*) by

72 per cent. sulphuric acid, (*d*) by 2 per cent. aqueous alcoholic caustic soda and (*e*) by hydrochloric acid and phosphorus pentoxide. All these methods have been tried one after another in the case of jute—they are described in detail in the following paragraphs.

(*a*) *By Caustic Soda under Pressure.*—In her studies on lignification Mehta (*loc. cit.*) investigated thoroughly the alkali process for the isolation of lignin and found that treatment with 4 per cent. caustic soda under 10 atmosphere pressure (185°) was the best method for the estimation of lignin in timbers. She considered that lignin isolated by this process suffered no internal change whatsoever, it was homogeneous and the resolution was complete in one hour. But the yield of lignin was in all cases lower than that by acid processes. It differed from all lignins described previously in that it was soluble in fairly large number of organic solvents, and had a definite melting point. The method at first sight appeared to yield a lignin in more or less pure form and was therefore tried first of all.

5 G. of finely cut purified jute were taken in a glass vessel, mixed with 100 c.c. of 4% caustic soda and heated in an autoclave at 185°, under 10 atmosphere pressure for one hour. The contents were then cooled, filtered to a measuring flask and the residual cellulose washed with water until the washings were colourless. The volume was made up to 250 c.c. Fifty c.c. of the deep brown liquor were taken in a beaker, and the lignin was precipitated by adding sufficient strong hydrochloric acid. The precipitate was allowed to settle, filtered through an ordinary filter paper, and washed until the washings were free from chloride (silver nitrate test). The washings were always light brown, indicating that the substance was partly soluble in water. By washing with hot water, a filtrate of deeper colour was obtained; it being more soluble in hot water. Lignin was then purified by dissolving in 95 p. c. boiling alcohol and evaporating off the solvent subsequently on water-bath. It was dried at 110° and weighed. The yield was never concordant; it varied between 2·7 and 3·4 per cent. depending upon the number of washings with water. The figure is too low to be accepted, as the percentage of lignin in jute has been previously found to be about 15 p. c. by chlorine peroxide method and by the method of Willstätter and Zechmeister (*Ber.*, 1918, **46**, 2401).

Lignin obviously suffered decomposition so as to give water-soluble products. It might be due to the concentration of the

alkali and the high pressure employed. The resolution of lignin was then carried out with 1% alkali and under 5 atmosphere pressure. The percentage was about 4·4, but the resolution was never complete; lignin could be further obtained from the residual cellulose by the acid process. The lignin, as before was partially soluble in water. The drawback of this process has also been recently shown by Dorée and Barton-Wright (*Biochem. J.*, 1927, 21, 290) who following strictly Mehta's method, could obtain only 18·6 p. c. lignin, 7·3 p. c. being soluble in water and 3·7% remaining with the cellulose, making a total of 29·6%. They obtained a simpler product ($C_{20}H_{20}O_6$) having a fixed melting point, and named it "meta-lignin". As my primary concern was to obtain lignin from jute in the form in which it exists in jute, this method had to be abandoned. But it is interesting to note here that the "lignin" obtained from jute does not melt below 300°; it is a deep brown amorphous substance, obtained as a glistening solid on the evaporation of alcohol. It is soluble in glacial acetic acid, pyridine, acetone, aniline, in the cold; but insoluble in benzene, ether, carbon disulphide, carbon tetrachloride and slightly soluble in boiling nitrobenzene and chloroform. No trace of sodium could be found in the lignin showing that sodium has not entered the lignin molecule. It gives no ash. It reduces Fehling's solution quite readily. With chlorine in carbon tetrachloride suspension, a deep yellow product is obtained, hydrochloric acid being simultaneously evolved; substitution evidently takes place. It has no aromatic odour like vanillin. It gives no furfural showing the absence of pentosans. But it gives a small amount of carbon dioxide when distilled with 12 p. c. hydrochloric acid, showing perhaps the presence of a carboxyl group, part of which might have been lost during isolation, as otherwise it is difficult to explain the evolution of carbon dioxide. It gives 20·1 p. c. methoxy (by Zeisel's method). An acetyl compound is readily obtained with acetic anhydride and a few drops of strong sulphuric acid, at 80°, showing the presence of hydroxyl groups.

(*b*) *Hydrochloric Acid Process.*—The use of fuming hydrochloric acid (42 p. c. in the isolation of lignin from ligno-celluloses was first proposed by Willstätter and Zechmeister (*loc. cit.*) and this method has been employed more than any other for the determination of lignin by many investigators during the last few years. The following procedure was adopted for the estimation of lignin from jute.

42 p. c. Hydrochloric acid (*d* 1·21) cannot be obtained in the market. Passing hydrochloric acid gas into jute suspended in strong hydrochloric acid cooled in ice, was found quite unsatisfactory. The following method was, however, found suitable.

Dry hydrochloric acid gas was passed into Merck's fuming hydrochloric acid (*d* 1·175) contained in a gas-washer which was cooled with ice and common salt until the density rose up to 1·21. One g. of very finely cut jute (of known moisture content) was taken in a well fitted glass stoppered bottle (250 c.c.); 50 c.c. of the prepared hydrochloric acid were quickly introduced and the stoppered bottle was shaken vigorously for about 15 mins. holding the stopper tightly. The stopper was kept under pressure so that the hydrochloric acid gas might not escape. Twelve hours at room temperature were found to be quite sufficient for the acid to dissolve the cellulose completely. The lignin obtained is deep black instead of light grey if the exposure be prolonged. It is important to note here that 40 p. c. hydrochloric acid does not dissolve the cellulose completely even when it is allowed to act for 48 hours. Traces of jute taken remain undissolved even with 42 p. c. hydrochloric acid if not shaken occasionally. The whole was then poured into a large volume of water and the contents of the bottle washed off into the beaker. The acid was diluted to about 7-8 p. c. and the whole boiled for ½ hour. There is considerable difficulty in filtering the lignin owing to the colloidal nature of the solution, if this last operation is omitted. It was filtered hot through asbestos in a Gooch crucible, washed repeatedly with boiling water until the washings were neutral to litmus. It was then dried at 110° and weighed. The results obtained are fairly concordant, the mean value being 15·43 p. c. (calculated on dry jute).

The lignin was obtained as a light spongy mass of grey colour. In order to determine the percentage of undissolved cellulose if any, a weighed quantity of finely powdered lignin was suspended in water in a gas washer and chlorine peroxide gas was passed through the washer, for about 16 hours. The lignin was dissolved by the chlorine peroxide. The whole was filtered through a glass filter, dried at 110° and weighed. The residue amounted to 0·13. p. c. But this was not cellulose, as most of it dissolved in strong hydrochloric acid and Ca, Mg, and Fe were detected in the solution. The rest was silica. Thus it must be attributed to the ash-giving bodies present in lignin; and not to any undissolved cellulose.

The lignin gives no furfural showing the absence of pentosans. It does not melt below 300° and is insoluble in all organic solvents. It is very slightly soluble in caustic soda, pyridine and ammonia. It gives 0·18 p. c. ash and 16·4 p. c. methoxy (Zeisel). It also gives carbon dioxide (1·557) when distilled with 12 p. c. hydrochloric acid and reduces Fehling's solution readily and gives a yellow chloro-derivative, with the evolution of hydrochloric acid when chlorine is passed in carbon tetrachloride suspension. The chloro-lignin is soluble in dilute alkalis, alcohol, pyridine, acetone, it does not melt below 300° and reduces Fehling's solution. It contains 27·87 p. c. chlorine (Carius). This lignin is readily oxidised by alkaline hydrogen peroxide and strong nitric acid to water-soluble products.

Attempts to acetylate this lignin with acetic anhydride and strong sulphuric acid, or sodium acetate (anhydrous), with acetyl chloride alone, and with pyridine were only partially successful as only a small yield of acetyl compound was obtained. Better results were obtained by prolonged heating with acetic anhydride and zinc chloride under reflux at 130-40°. The acetyl lignin (5·78 p. c. acetyl, Perkin's method) is a deep brown amorphous substance, soluble in pyridine, alkalis and glacial acetic acid but insoluble in sodium carbonate solution.

It was difficult to remove the last trace of hydrochloric acid from the lignin—the aqueous washings were neutral to litmus but gave test for chloride with silver nitrate. The mass being spongy a small amount of hydrochloric acid was tenaciously retained by it and only repeated treatment with boiling water under reflux, could effect complete removal. The comparatively higher values obtained by Willstätter process are often ascribed to the combination of lignin with hydrochloric acid; but the absence of chlorine in the lignin thus obtained does not support this view.

The lignin being insoluble in all media, it was not possible to purify it further. Lignin, if it be purely an organic compound, should give no ash. But it has not yet been possible to obtain ash-free lignin by acid hydrolysis. Phillips (*J. Amer. Chem. Soc.*, 1929, **51**, 2420) obtained a lignin from corn cobs by hydrochloric acid method, whose ash content was 1·05%. This ash must be due to the presence of impurities associated with the original ligno-cellulose or lignin itself is an organo-metallic compound. The former however, appears to be more probable in view of the fact that the percentage is too low, and that more than one metal have been detected in

the ash, which is never constant in percentage. Attempts are being made to remove these impurities so as to obtain lignin in the pure form suitable for ultimate analysis.

(*c*) *Sulphuric Acid Method.*—Probably the oldest and most commonly used method for the estimation of lignin is due to Klason (*Ber. der Vereins der Papier u. Zellstoffchemiker*, 1908, pp. 52-53) who hydrolysed finely divided wood with 70% sulphuric acid at room temperature. The polysaccharides dissolved and lignin remained insoluble. König (Dissertation, 1914, Munster) modified this method by recommending the use of 72% sulphuric acid. Lignin from jute was estimated in the following way:

1 G. of finely cut jute was treated with 25 c.c. of 72% sulphuric acid in a stoppered bottle, and the two were intimately mixed with a glass rod causing the jute to become completely disintegrated. The bottle was shaken occasionally and kept at room temperature for 16 hours, after which the acid was diluted with water to about 3%, boiled for half an hour and filtered hot through a Gooch crucible. The precipitate was washed free from acid by hot water, dried at 110° and weighed. Filtration even after boiling was very tedious: repeated washings with hot water for two days were required to make it acid-free. The yield was 18·2% (calculated on dry jute).

The lignin obtained is a very pasty deep black mass, which on drying gives a heavy solid, difficult to powder. Like the hydrochloric acid lignin, it is insoluble in all common solvents and alkalis. It does not melt even at 300°. It gives 0·31% ash, 13·5% methoxy, contains no sulphur, reduces Fehling's solution, gives carbon dioxide on distillation with 12% hydrochloric acid, but no furfural. Only partial acetylation could be effected by acetic anhydride and zinc chloride. It contains no undissolved cellulose. When heated under 10 atmosphere pressure with 4% caustic soda for one hour it dissolved in the alkali and gave a precipitate with hydrochloric acid which is slightly soluble in water. In other respects also it is identical with the alkali lignin. With chlorine in carbon tetrachloride a yellow chloro-derivative is obtained.

(*d*) *Alcoholic Caustic Soda Process.*—Beckmann, Liesche and Lehmann (*Z. angew. Chem.*, 1921, **34**, 285) employed 2% caustic soda in aqueous alcoholic solution acting in the cold for 48 hours for the isolation of lignin from rye straw. The alcohol prevented the solution of hemi-celluloses, pentosans and other non-lignified substances soluble in aqueous alkali. In the case of jute, 50 g. of finely cut jute

were treated with 250 c.c. of 2% alcoholic caustic soda (5 g. caustic soda, 100 c.c. water and 150 c.c. alcohol-95%) and allowed to stand at room temperature for 24 hours. The filtered solution was neutralised with hydrochloric acid and alcohol was distilled off under reduced pressure. The aqueous solution was acidified with hydrochloric acid and the precipitated lignin was filtered off. There was considerable difficulty in filtration due to the colloidal nature of the lignin. The yield was very poor being only 1·3%. By a second treatment a further yield of 0·6% was obtained. It is a light yellow powder, soluble in alcohol. Least drastic though the conditions of isolation, obviously it cannot be employed for the quantitative estimation of lignin. It was therefore discarded.

(*e*) *With Hydrochloric Acid and Phosphorus Pentoxide.*—Wenzl (*Papierfabr.*, 1924, **22**, 101) employed fuming hydrochloric acid (*d* 1·19) mixed with phosphorus pentoxide for the estimation of lignin. 30 G. of the oxide were gradually added to 100 c.c. of the acid while cooling in ice. 1 G. of jute was digested with 25 c.c. of this mixture for 16 hours at room temperature in a stoppered phial. The solution was then diluted with water, boiled for about half an hour, filtered and the lignin dried and weighed. The yield and physical and chemical properties are all similar to the hydrochloric acid lignin. In fact, it is no new method and the results obtained are not different.

Of all the five methods tried for the isolation and estimation of lignin from jute, Willstätter's method was found to be the best. In the sulphuric acid process, the higher yield has been ascribed to the formation of humus (Paloheimo, *Biochem. Z.*, 1925, **165**, 463) and to the absorption by lignin of secondary products. The percentage of methoxy is lower, a fraction of the methoxy groups has been lost in the process of isolation. The ash content is lower in the hydrochloric acid process (0·13%) than in the sulphuric acid process (0·31%). The estimation of lignin by difference with chlorine peroxide which has been shown by Chowdhury and Majumdar (*J. Indian Chem. Soc.*, 1929, **6**, 239) to have almost no effect on other constituents of jute, give the figure, 15·2% (obtained by the present worker) which is in close agreement with that obtained by the hydrochloric acid process.

My best thanks are due to Dr. J. K. Chowdhury for his keen interest and valuable suggestions and to Prof. J. C. Ghosh for giving every facility to carry out this work.

Chemical Laboratory,
Dacca University.

Received May 4, 1931.

Synthesis of Coumarins from Phenols and β-Ketonic Esters using Phosphorus Pentoxide. Part II. Coumarins from Polyhydric Phenols and α-Naphthol.

By Dukkhaharan Chakravarti.

In an earlier part of this work (Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 129) it has been shown that resorcinol reacts with ethyl acetoacetates to form a coumarin and not a chromone even in presence of phosphorus pentoxide, which favours chromone formation (Petscheck and Simonis, *Ber.*, 1913, **46**, 2015; Simonis and Lehmann, *Ber.*, 1914, **47**, 697; Simonis and Remmert, *ibid.*, p. 2229).

The condensation of polyhydric phenols, *e.g.* orcinol, pyrogallol, phloroglucinol and also of α-naphthol with ethyl acetoacetates using phosphorus pentoxide has been studied in this work and the products obtained in these cases are also coumarins and not chromones. These phenols also condense most readily in the cold with much rise of temperature with ethyl acetoacetates in presence of phosphorus pentoxide and the condensation products are in all cases identical with the coumarins, prepared using sulphuric acid according to Pechmann's method, as is proved by their mixed melting points and also by the identity of their derivatives.

It is interesting to observe that orcinol condenses with the ethyl acetoacetates in presence of sulphuric acid to form products, which are soluble in alkali without any fluorescence unlike the 7-hydroxycoumarins and hence they are probably 5-hydroxycoumarins as was shown by Dey (*J. Chem. Soc.*, 1915, **107**, 1646).

The causes of the coumarin and chromone formation in these condensations are being investigated and the results of the condensation of monohydric phenols with β-ketonic esters using phosphorus pentoxide will be communicated in due course.

Experimental.

Coumarins from Orcinol.

5-Hydroxy-4:7-dimethylcoumarin (β Methylhomoumbelliferone).—Phosphorus pentoxide (18 g.) is gradually added to a mixture of

orcinol (5 g.) and ethyl acetoacetate (5 g.) cooled in ice. Vigorous reaction sets in in the cold with much evolution of heat. When the reaction ceases, the cold mass is treated with water and the solid is washed with water and crystallised from dilute alcohol (charcoal) as colourless needles, m. p. 248°; the melting point is not depressed when mixed with a specimen of the coumarin prepared by Pechmann and Cohen's method (*Ber.*, 1881, **17**, 2187) using sulphuric acid.

The *acetyl* derivative crystallises from dilute alcohol in colourless needles, m. p. 195°. (The acetyl derivative of Pechmann and Cohen's coumarin also melts at 195°).

5-*Hydroxy-3-chloro*-4:7-*dimethylcoumarin* is prepaped by adding phosphorus pentoxide in the cold to a solution of orcinol and ethyl α-chloroacetoacetate in a few c.c. of alcohol. The cold mass is poured into water and the pasty solid is dissolved in cold caustic alkali, the alkaline solution extracted with ether and the aqueous solution acidified. The precipitate is washed with a solution of sodium bicarbonate and crystallised from rectified spirit in felted needles, m.p. 295°. The *acetyl* derivative crystallises from alcohol in long needles, m.p. 160°. It is identical with the compound prepared using sulphuric acid by Pechmann and Hanke (*Ber.*, 1901, **34**, 354).

5-*Hydroxy*-3:4:7-*trimethylcoumarin*, prepared in a similar manner from orcinol and ethyl α-methylacetoacetate (in alcohol), is isolated and purified as usual. Two products are obtained; one, is soluble in alkali with blue fluorescence and the other dissolves in alkali without any fluorescence. The non-fluorescent product is isolated on repeated fractional crystallisation from alcohol as cubes, m.p. 250°. (Found: C, 70·44; H, 5·93. $C_{12}H_{12}O_3$ requires C, 70·59; H, 5·88 per cent.). The *acetyl* derivative, prepared in the usual manner, crystallises from alcohol in needles, m.p. 135°. (Found: C, 68·20; H, 5·61. $C_{14}H_{14}O_4$ requires C, 68·29; H, 5·69 per cent.). The identical compound (m.p. 250°, acetyl derivative, m.p. 135°) is also obtained with sulphuric acid, there being no depression of the melting point when mixed with the other specimen.

5-*Hydroxy*-3-*ethyl*-4:7-*dimethylcoumarin* is prepared from orcinol and ethyl α-ethylacetoacetate and sulphuric acid. It crystallises from dilute alcohol or glacial acetic acid in needles, m.p. 206°. (Found: C, 71·48; H, 6·31. $C_{13}H_{14}O_3$ requires C, 71·56; H, 6·2 per cent.).

The interaction of orcinol and ethyl α-ethyl (or α-propyl or α-*iso*-propyl) acetoacetate in presence of phosphorus pentoxide leads to

two products in each case, both soluble in alkali, one with blue fluorescence and the other without any fluorescence and they could not be satisfactorily separated.

Coumarins from Pyrogallol.

7:8-*Dihydroxy-4-methylcoumarin* (*β-Methyldaphnetin*) is prepared by adding, in the cold, phosphorus pentoxide (18 g.) to a mixture of pyrogallol (5 g.) and ethyl acetoacetate (5 g). It crystallises from dilute alcohol (charcoal) as colourless needles, m.p. 235°, the melting point not being depressed when mixed with a sample of β-methyldaphnetin prepared by Pechmann and Duisberg (*Ber.*, 1883, **16**, 2119) with sulphuric acid.

7:8-*Dihydroxy-3-chloro-4-methylcoumarin* is obtained by adding phosphorus pentoxide to a solution of pyrogallol and ethyl α-chloroacetoacetate in a few c.c. of alcohol. It crystallises from alcohol in lustrous needles, m.p. 265°. The *acetyl* derivative crystallises in prisms from alcohol, m.p. 197°. It is identical with the 3-chloro-4-methyldaphnetin prepared by using sulphuric acid by Pechmann and Hanke (*loc. cit.*) ; no depression of the melting point is observed when the two are mixed.

7:8-*Dihydroxy*-3:4-*dimethylcoumarin* is prepared by condensing pyrogallol and ethyl α-methylacetoacetate using phosphorus pentoxide and finally heating for half an hour on the boiling water-bath. It is obtained as cubes (m.p. 270°) from glacial acetic acid. The yield is very poor in this case. The identical compound is obtained by using sulphuric acid as the condensing agent. The mixed melting point of the compounds is also 270°. (Found: C, 64·13; H, 4·92. $C_{11}H_{10}O_4$ requires C, 64·07; H, 4·85 per cent.).

7:8-*Dihydroxy-3-ethyl-4-methylcoumarin* is obtained by adding, in the cold, sulphuric acid (15 c.c.) to a mixture of pyrogallol (5 g.) and ethyl α-ethylacetoacetate (5 g.) and keeping the solution overnight. It crystallises from dilute alcohol as lustrous rhombic plates, m.p. 218°. (Found: C, 65·38; H, 5·52. $C_{12}H_{12}O_4$ requires C, 65·45; H, 5·45 per cent.).

It has not been possible to condense pyrogallol with ethyl α-ethyl- (or α-*iso*propyl-) acetoacetate in presence of phosphorus pentoxide even at a higher temperature.

Coumarins from Phloroglucinol.

5:7-Dihydroxy-4-methylcoumarin, *5:7-dihydroxy-3:4-dimethylcoumarin and 5:7-dihydroxy-3-ethyl-4-methylcoumarin* have been prepared by the condensation of phloroglucinol with ethyl acetoacetate, ethyl α-methylacetoacetate and ethyl α-ethylacetoacetate respectively in presence of phosphorus pentoxide but the experimental details are not given as they have already been described by Canter, Curd and Robertson (*J. Chem. Soc.*, 1931, p. 1255). It has been observed by the author that the addition of a little absolute alcohol is much advantageous.

5:7-Dihydroxy-3-chloro-4-methylcoumarin, prepared by adding phosphorus pentoxide in the cold to phloroglucinol and ethyl α-chloroacetoacetate dissolved in a little alcohol, is crystallised in needles from acetic acid. It melts with decomposition at 306-308°, the m.p. not being depressed when mixed with the coumarin, prepared with sulphuric acid by Dey's method (*J. Chem. Soc.*, 1915, **107**, 1648).

Coumarins from α-Naphthol.

4-Methyl-1:2-α-naphthapyrone is prepared by adding phosphorus pentoxide in the cold to a solution of α-naphthol and ethyl acetoacetate in a little alcohol. The product obtained on pouring the mass into water, is dissolved in boiling absolute alcohol (charcoal) from which on cooling beautiful needles melting at 167° separate. The mixed melting point of this compound and the coumarin prepared by Bartsch (*Ber.*, 1903, **36**, 1966) is also 167°.

3-Chloro-4-methyl-1:2-α-naphthapyrone is obtained by the interaction of α-naphthol, ethyl α-chloroacetoacetate in presence of phosphorus pentoxide. The product crystallises from glacial acetic acid, melts at 225-27° and is identical with the compound described by Dey (*loc. cit.*) there being no depression of the m.p.

3:4-Dimethyl-1:2-α-naphthapyrone, obtained by the condensation of α-naphthol and ethyl α-methylacetoacetate using phosphorus pentoxide, crystallises in shining needles from glacial acetic acid and melts at 197-99°. (Found: C, 80·42; H, 5·44. $C_{15}H_{12}O_2$ requires C, 80·35; H, 5·35 per cent.). The identical compound melting at 197-99° is also obtained by condensing α-naphthol, ethyl α-methylacetoacetate in presence of sulphuric acid. The mixed melting point is also 197-99°.

3-*Propyl*-4-*methyl*-1:2-α-*naphthapyrone* is prepared by the interaction of α-naphthol and ethyl α-propylacetoacetate using sulphuric acid. It crystallises in needles from rectified spirit, m.p. 118°. (Found: C, 80·88; H, 6·41. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·35 per cent.). No definite product could be isolated by using phosphorus pentoxide.

3-iso*Propyl*-4-*methyl*-1:2-α-*naphthapyrone* is obtained from α-naphthol and ethyl α-*iso*propylacetoacetate using sulphuric acid in the usual manner. It crystallises in needles from rectified spirit, m.p. 165°. (Found: C, 80·99; H, 6·21. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6 35 per cent.). No definite product has been isolated by using phosphorus pentoxide.

The author desires to express his grateful thanks to Prof. R. N. Sen for his advice and keen interest in this investigation.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Received June 29, 1931.

Studies in Alcoholysis. Part I.

By M. Goswami and S. Ramanujam.

Replacement of one alcoholic group by another in esters has been studied in detail.* Haller (*Compt. rend.*, 1906, **143**, 657), whose experiments confirmed the views of Lewkowitsch (*J. Soc. Chem. Ind.*, 1903, **22**, 592), converted glycerides into methyl esters of the constituent fatty acids by treating them with methyl alcohol in the presence of hydrochloric acid. The alcoholysis occured in stages as was found by Grun (*Chem. Zentr.*, 1919, **I**, 222).

It has been found by Haller and other workers that alcoholysis proceeds easily up to the glycerides of C_{12}- acid after which it becomes irregular and upon this observation Fendler (*Mitt. a. d. Pharm. Institut der Univ. Berlin*) apparently has tried to base his "distillation value" calculated from the results of "ethanolysis" by which he proposes to determine the percentages of cocoanut oil (which has a higher Polenske value and as such should yield greater quantity of ethyl laurate in the process of alcoholysis) in butter fat.

The problem of detection of cocoanut oil in butter fat is in reality a very intricate one and it has been found in practice that adulteration with a small percentage of cocoanut oil, especially if backed by lard or tallow, hardly affects the wide ranges of the different values of butter fat. It was thought that if some suitable catalyst other than hydrochloric acid could be found, which would effect selective "alcoholysis" on C_{12}-glycerides then such sort of detection of adulteration, although lengthy, would be a sure one.

With this idea the present work was begun and the following new catalysts were tried:—Benzenestearosulphonic acid, naphthalene-

* Kolhatkar, *J. Chem. Soc.*, 1915, **107**, 921 ; Sudborough and Bhagwat, *J. Indian Inst. Sci.*, 1918, **2**, 121; Sudborough and Karvel, *J. Indian. Inst. Sci.*, 1919, **3**, 1; Darsanacharyya and Sudborough, *J. Indian Inst. Sci*, 1921, **4**, 181; Goldschmidt, Gorbitz, Hougen and Pahle, *Z. physikal. Chem.*, 1921, **99**, 116.

stearosulphonic acid (Twitchell's reagents), pyridine, piperidine. piperidine hydrochloride and phosphorus oxychloride. The results so far obtained have not fulfilled the expectation of selective alcoholysis but it has been found that phosphorus oxychloride can form a convenient substitute for hydrochloric acid. The results are comparable. In the Haller's hydrochloric acid method, the acid gas is required to be pure and dry and there are additional manipulative difficulties with regard to exact increase in weight and moreover when the ether-alcoholic solution is heated on the water-bath the amount of the catalysts must inevitably suffer loss in weight, as, much of the acid escapes. But in the case of phosphorus oxychloride the required amount may be added at once and proper check may be made strictly with accurate weight of the catalyst. As this method may simplify in future the alcoholysis of numerous unexamined oils, the results obtained are published.

It was observed that under proper precautions benzenestearosulphonic acid and naphthalenestearosulphonic acid do not cause any appreciable alcoholysis, if traces of mineral acids are carefully excluded. Alcoholysis observed by Hallen with phenolsulphonic acid is probably due to the presence of traces of mineral acid. Clarification of this issue, as also the action of other catalysts will be the subject of a future communication.

Experimental.

Preparation of Benzenestearosulphonic Acid.—To a mixture of 30 c.c. of benzene and 30 c.c. of oleic acid, a large excess of concentrated sulphuric acid was added slowly avoiding rise in temparature. After several hours the reaction mixture was boiled with water, the lower layer was removed, the upper layer being washed by water containing hydrochloric acid till it was free from sulphuric acid. The mixture was then dissolved in ether and shaken with water. The aqueous extract was then treated with a little hydrochloric acid (the reagent is insoluble in water acidulated with hydrochloric acid), taken up with ether, again extracted with water and the water evaporated off; the hydrochloric acid is then completely removed by heating in an air-oven at 100° for several hours (Twitchell, *J. Amer. Chem. Soc.*, 1900, 22, 22).

Preparation of Naphthalenestearosulphonic Acid.—Oleic acid (100 parts) was placed in a dry vassel with naphthalene (30 parts),

the mixture being warmed till solution took place. It was then cooled to 50° by stirring in order to prevent the naphthalene settling out as a solid mass at the bottom. Sulphuric acid (66° Bé, 300 parts) having 99·2 p. c. sulphuric acid, was run in at first drop by drop to avoid violent reaction taking place and the mixture was well stirred. The temperature kept below 50°. When all the acid had been added the mixture was poured into twice the volume of cold water, well-stirred and allowed to settle overnight. The reagent appeared as a thick layer at the top of the water, which was then separated and dried in air-oven (Twitchell, *loc. cit.*, p. 25).

Alcoholysis.—In each case 50 c.c. of cocoanut oil well dried over anhydrous sodium sulphate were taken; this was mixed with 125 c.c. of anhydrous ether (kept for a fortnight over sodium wire and distilled) and 75 c.c. of anhydrous methyl alcohol (dried over quick lime and distilled) and boiled under reflux gently with the catalyst on the water-bath for 4 hours. In the case of hydrochloric acid gas it was first of all dried by concentrated sulphuric acid and passed through methyl alcohol until the requisite weight was gained. The other catalysts were first accurately weighed and then added to methyl alcohol a little at a time.

After the reaction (after 4 hours) the ether alcoholic solution of the esters was neutralised (excepting in the cases of pyridine, piperidine and piperidine hydrochloride) with barium carbonate with constant shaking. The ether and methyl alcohol were then distilled off and the residue in the flask was taken up with ether. The ethereal solution was repeatedly washed with brine to remove glycerol, excess of barium carbonate, etc., and then dried over freshly ignited anhydrous magnesium sulphate overnight. The magnesium sulphate was filtered off through a Gooch and washed with dry ether; the collected ethereal solution was then distilled on the water-bath to drive away ether and the residual liquid was then fractionated at 16-17 mm. pressure. The fractions were collected at ranges comprising approximately the midpoints between the boiling points of the esters at 15-17 mm. pressure which are as follows:-

	B. p. at 15-17 mm.		B. p. at 15-17 mm.
Methyl caproate	52·5°	Methyl laurate	141°
,, caprylate	83°	,, myristate	167·5°
,, caprate	114°	,, palmitate	176°

TABLE I.

Catalysts used.	Amount of catalyst taken.	Methyl esters collectedat 15 17 mm. Up to 100°.	100°-30°.	130°-55°.	155°-88°.
Benzenestearosulphonic acid containing traces of hydrochloric acid.	1·72 g.	1·5 c.c.	2·5 c.c.	7·8 c.c.	—
Benzenestearosulphonic acid free from hydrochloric acid.	2·95	0	0	2	—
Pyridine	1·72	—	—	—	Practically nil.
Piperidine	1·7	0·5	1	8	—
Piperidine hydrochloride	1·72	0	0	0	Practically nil.
Hydrochloric acid gas	2·95	3	9	26·2	9·2 c.c.
Phosphorus oxychloride	2·95	4·2	7·2	26·5	9·2

TABLE II.

	Catalysts used.	Amount of catalyst taken.	Methyl esters collected at 16-17 mm. Up to 100°.	100-30°.	130-55°.	155-88°.
I.	Naphthalenestearosulphonic acid containing traces of sulphuric acid.	3·57 g.	2 c.c.	6 c.c.	10 c.c.	8·5 c.c.
II*	,,	1·72	0	0	0·75	1·2

* Contained different amount of sulphuric acid.

TABLE III.

Catalysts used.	Amount of taken.	Methyl esters collected at 15-17 mm. catalyst Up to 100°.	100-30°.	130-55°.	155-83°.
Hydrochloric acid gas	3·56 g.	3 c.c.	11 c.c.	26 c.c.	9·5 c.c.
Phosphorus oxychloride	3·56	3	10·5	24·5	8·5

APPLIED CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
CALCUTTA.

Received May 7, 1931.

Introduction of Arsenic into Coumarin Nucleus. Part I.

By M. Goswami and H. N. Das-Gupta.

No attempt appears to have hitherto been made to introduce arsenic into coumarin nucleus by any of the general methods, *e.g.*, Bart's reaction (D. R. P. 250264) or Roeder and Blasi's method (*Ber.*, 1914, 47, 2748). In view of the well-known facts that sodium cinnamate and sodium *o*-coumarate (Hetol) augment the number of polymorphonuclear white blood corpuscles and thereby help in checking tuberculosis, and that the group -O-CO- present in many drugs is supposed to be responsible for increasing internal secretions, the combination of the coumarin molecule, which possesses these groupings, with the therapeutically active pentavalent arsenic atom appeared to us to have great potentialities as a drug.

The introduction of arsenic by the method of Roeder and Blasi failed because the coumarin mercuri-chloride was found to be decomposed by arsenic chloride regenerating coumarin. In this connection we wish to record the fact that the coumarin mercuri-chloride required for Roeder and Blasi's reaction, which was prepared from coumarin and mercuric acetate by Dimroth's method (*Ber.*, 1898, 31, 2154), did not offer any of the peculiar difficulties in its preparation which appear to have been encountered by Sen and Chakravarti (*J. Indian Chem. Soc.*, 1929, 6, 847).

The application of Bart's reaction to 6-aminocoumarin, however, led to the formation of an arsenic derivative crystallising from acetic acid as a yellow microcrystalline solid, melting and decomposing at 200°. The analytical figures both for arsenic, carbon and hydrogen are in agreement with those required for tricoumarylarsenic oxide of the formula: $(C_9H_5O_2)_3As:O$.

The compound, like triphenylarsenic oxide and other similar bodies, dissolves in alkalis and alkaline carbonate and is reprecipitated by acids.

As the employment of arsenious oxide and sodium carbonate according to the original Bart's method led to much frothing and the formation of considerable amount of tarry matter, the reaction was modified by using a solution of arsenic trichloride in hydrochloric acid when the reaction proceeded smoothly and gave a good yield (about 55 per cent.) of the product

The compound has been examined for finding out the maximum and minimum lethal doses.

Experimental.

Mercuration of Coumarin.—Coumarin (10 g.), 96 per cent. acetic acid (100 c.c.) and freshly prepared mercuric acetate (12 g.) were taken in a stout flask and heated under pressure in an oil-bath at 140-50° for five hours. After cooling the mixture was filtered and the residue washed with acetic acid. The filtrate and washings were evaporated to a small volume and treated with alcoholic calcium chloride to convert the acetate into the less soluble chloride. This was filtered and the product washed successively with water, hot water, alcohol and ether, the latter solvent being used to remove any unchanged coumarin. The coumarin mercuri-chloride thus obtained was dried in a vacuum desiccator (yield 50 per cent.).

The compound decomposes at 178°. The properties of this compound are identical with those recorded by Sen and Chakravarti. (Found: Hg, 52·01, 51·95. $C_9H_5O_2Cl\,Hg$ requires Hg, 52·55 per cent.).

Introduction of Arsenic into the Coumarin Nucleus.—The following are some of the attempts to introduce arsenic into the coumarin nucleus *via* coumarin mercuri-chloride:

(*a*) A mixture of coumarin mercuric-chloride (4 g.) and arsenic trichloride (10 g.) was heated in a pressure flask on a water-bath for 5 hours. The whole was then allowed to settle for two days when crystals of mercuric chloride settled at the bottom and the supernatant liquid consisted of two layers. The upper one was colourless, whilst the lower one was brown. The latter was separated from mercuric chloride and subjected to distillation under reduced pressure. The first fraction collected at 94-95° was reddish in colour which on chlorination and subsequent treatment with water resulted in the dissolution of the oily layer with rise in temperature. The second portion collected between 98° and 105° was similarly

treated and this resulted in the precipitation of a crystalline mass which on examination was found to be arsenious oxide.

(*b*) A mixture of coumarin mercuri-chloride (5 g.) and arsenic trichloride (17 g.) was heated in absence of air at 140-50° for 4 hours. There were formed two layers and a precipitate of mercuric chloride. Each layer on distillation under reduced pressure followed by chlorination and treatment with water gave no arsenic derivative of coumarin.

(*c*) A mixture of coumarin mercuri-chloride (11 g.) and arsenic trichloride (35 g.) was heated under reflux over a direct flame for 5 hours and the resulting liquid was allowed to settle overnight. The white precipitate collected at the bottom was separated by filtration through glass wool and the filtrate subjected to vacuum distillation. The fraction collected at 60-62°/17-18 mm., on analysis, was found to be arsenic trichloride. The residue in the distilling flask became pasty. This was treated with ether whereby a small portion went into solution. The ethereal extract on evaporation and treatment with water and chlorine was found to give coumarin. The residue in the flask was mercuric chloride.

(*d*) Coumarin mercuri-chloride (14 g.) and arsenic trichloride (25 g.) were heated on a water-bath for 4-5 hours and was allowed to stand overnight. The clear solution was next subjected to distillation which began at 140° and continued up to 270°. The distillate on examination was found to be arsenic trichloride and the white residue in the distilling flask nothing but coumarin.

(*e*) The solution obtained by heating coumarin, mercuric-acetate, and acetic acid was filtered and was treated with arsenic chloride in the cold ; a white precipitate was produced which was washed with cold acetic acid to dissolve mercuric acetate and then with warm water. On examination it was found to be coumarin mercuri-chloride.

Tricoumaryl Arsenic Oxide.—(*i*) Arsenious oxide (24 g.) was dissolved in sodium carbonate (32 g. in 800 c.c. water) solution with the application of heat ; to this copper sulphate (0·7 g.) was added. The mixture was cooled to 0° in a vessel provided with a mechanical stirrer and to this a diazotised solution of 6-aminocoumarin (16 g. of amino-compound, 20 c.c. hydrochloric acid in 60 c.c. of water and 7 g. of sodium nitrate in 20 c.c. of water) cooled to 0° was gradually added during the course of 1 hour. Vigorous frothing which is usual in such reactions was partially avoided by adding

a little benzene and increasing the speed of rotation of the stirrer. The stirring was continued for one hour after the addition of the diazotised solution. The product was then allowed to stand overnight. The mass was then filtered ; the filtrate was evaporated to one third of the orig inal volume, boiled with animal charcoal and filtered again. To the filtrate strong hydrochloric acid was added gradually when most of the tarry matter separated ; it was filtered and the filtrate was finally acidified when the tricoumaryl arsenic oxide was precipitated as a dark brown mass. This on being repeatedly crystallised from acetic acid was obtained as a light yellow microcrystalline mass melting with slight decomposition at 200°

(*ii*) *By Modified Bart's Process.*— 6-Aminocoumarin (10 g.) dissolved in hydrochloric acid (25 c.c. in 40 c.c. of water) was diazotised with a solution of sodium nitrite (4·5 g. in 20 c.c. of water) the temperature being kept near 0° and to this copper sulphate (0·5 g.) was added. In three separate vessels arsenic trichloride (14 g.), water (25 c.c.) and hydrochloric acid (25 c.c.) were taken, each cooled initially to 10° and then mixed together, and the mixture thus obtained was added drop by drop to the well-cooled diazo-solution with stirring. The resulting solution was kept overnight and then filtered. The filtrate, light yellow in colour, was made alkaline with sodium hydroxide solution when a precipitate was formed which redissolved in excess of alkali to a dark brown solution. This was concentrated, boiled with animal charcoal and filtered. The filtrate on being acidified produced a precipitate which was twice crystallised from acetic acid. It was light yellow in colour and its melting point and percentage of arsenic were found to be identical with those of the previous compound obtained by Bart's method. The mixed m.p. was also 200°.

Tricoumaryl arsenic oxide prepared by both the methods is soluble in acetic acid but sparingly soluble in acetone and insoluble in all other organic solvents. It dissolves in ammonia, caustic alkalis and sodium carbonate solution with a reddish-brown colour from which acids precipitate the oxide.

The reaction probably takes the following course :—

$$(a)\quad 6\,C_9H_5O_2NH_2 \longrightarrow 6C_9H_5O_2{\cdot}N{:}N{\cdot}ONa \xrightarrow{(3AS_2O_3+15Na_2CO_3)} \longrightarrow (C_9H_5O_2)_3As(ONa)_2 + 4AsO(ONa)_3 + 5CO_2$$

(*b*) $(C_9H_5O_2)_3As(ONa)_2 + 2HCl \longrightarrow (C_9H_5O_2)_3As{=}O$

(Found: C, 59·87, 59·99; H, 3·02; As, 13·8, 13·85, 13·9. $C_{27}H_{15}O_7As$ requires C, 61·50; H, 2·80; As, 14·2 per cent.). The estimation of arsenic was carried out by the methods of Norton and Koch (*J. Amer. Chem. Soc.*, 1905, **27**, 1247) and of Ewins (*J. Chem. Soc.*, 1916, **109**, 1356).

The following toxicological tests were carried out by Mr. P. B. Sen, M. Sc., Lecturer in Biochemistry, Calcutta University, to whom our best thanks are due.

The toxicity of the sodium salt of the compound was determined and was found to be in the normal range as will be evident from the following table. The strength of the solution, which contained 0·85 per cent. of common salt, was 2 per cent.

Amount injected per kg.	Weight of the rat.	Vol. of the solution	Remarks.
0·04 g.	105 g.	0·21 c.c.	Survived
0·06	95	0·29	,,
0·07	55	0·19	,,
0·08	91	0·37	,,
0·09	96	0·43	,,
0·26	110	1·44	,,
0·28	85	1·19	,,
0·30	84	1·24	,,
0·30	126	1·94	,,
0·33	126	1·08	,,
0·35	100	0·87	,,
0·35	135	1·18	,,
0·35	60	0·52	Proved fatal †
0·37	90	0·83	,, *
0·37	140	1·28	Survived
0·37	145	1·30	Proved fatal *
0·39	30	0·29	,,
0·39	30	0·29	,,
0·39	35	0·339	,,
0·40	43	0·86	,,
0·40	85	1·70	,, ‡

* After 12 hours.
† After 24 hours.
‡ After 36 hours.

Thus it may be seen that the maximum and minimum lethal doses are comparable to those of soamin and are respectively 0·39 and 0·84 g. The therapeutic activity is being examined by Dr. A. C. Ukil of Indian Research Fund Association.

The investigation is being continued with substituted coumarins and naphthacoumarins.

APPLIED CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY, CALCUTTA.

Received May 5, 1931.

A New Method for the Characterisation and Estimation of Oils and Fats.

By J. K. Chowdhury and S. M. Das-Gupta.

It will generally be admitted that the present methods of fat analysis are quite unsatisfactory both for qualitative and quantitative purposes when mixtures of different oils and fats are concerned. It is thus a matter of great difficulty to detect and estimate adulterations in ghee (clarified butter fat) and other edible fats when these adulterations are made in an ingenious manner to baffle the physical and chemical tests usually employed by the analysts. Further, the usual tests are often unmethodical and extremely laborious and sometimes lead to unreliable results. Thus the colour and solubility tests used for qualitative purposes are often unreliable and misleading, though simple in nature. A rapid and reliable method for detection and estimation of oils and fats in mixtures is, therefore, a great necessity from analytical point of view. In the following investigations, a method has been developed for the characterisation of oils by subjecting them to the action of potassium permanganate under anhydrous conditions in the presence of an inert common solvent, when it has been found that the temperature of carbon dioxide evolution as well as the quantity of carbon dioxide evolved are constants for each individual oil within narrow limits and serve as an useful means not only for the detection of oils and fats in a mixture but also to get an idea of the approximate quantities present.

Oils and fats have been oxidised by several investigators by aqueous or acidic permanganate but under such conditions intimate contact of the molecules of the reagent with those of the fat cannot be expected, the latter being insoluble in water. It was therefore thought advisable to use an inert common non-aqueous solvent for

the oil as well as the oxidising agent. Such a method of oxidation has also been used by Hilditch and Lea (*J. Chem. Soc.*, 1927, 3106) who used acetone as a common solvent. It was, however, found in the course of these investigations that acetone is partially oxidised when heated with powdered potassium permanganate, thus vitiating the carbon dioxide values. For similar reasons glacial acetic acid was also found to be unsuitable. Pyridine has, however, been found to be most satisfactory as experiments revealed that when heated under identical conditions pyridine (Merck) remains unchanged up to 85° while between 85° and 100° only a small amount of carbon dioxide (0·0022%) is evolved. The solubility of permanganate was also found to be greater in pyridine than in acetone. The high boiling point of pyridine was a further advantage as a solvent, for, if carried over in the baryta-tubes used for carbon dioxide determinations, it would necessarily interfere with the results obtained. For the oxidation of oils and fats, the method of Hilditch and Lea (*loc. cit.*) has generally been followed with certain modifications to suit the estimation of carbon dioxide evolved. A detailed description of the method is given in the experimental section of this paper.

Some of the applications of this method of characterisation are noted below.

(*a*) *Differentiation of Drying, Semi-drying and Non-drying Oils.*— It is well-known that the iodine value is quite unreliable as a test of the drying nature of an oil, for several oils with high iodine value are known to be non-drying in nature. The following method of distinguishing drying, semi-drying and non-drying oils may, therefore, be found useful.

When shaken with pyridine and powdered potassium permanganate, a drying oil (*e.g.*, linseed oil) rapidly becomes very viscous and often semi-solid, while semi-drying oils (*e.g.*, sesame oil) becomes only partly viscous and non-drying oils remain quite fluid. It may be noted that fish oils though possessing high iodine value remain quite fluid when subjected to the above tests.

(*b*) *Rapid Determination of Unsaturation of an Oil.*—The degree of unsaturation of an oil may also be approximately determined in a rapid manner as follows:—

When an oil is shaken with pyridine and permanganate at room temperature, it is slowly oxidised with separation of manganese

dioxide and consequent blackening of the colour. It has been found that the time required for blackening is dependent on the unsaturation of the fat, the higher the unsaturation the less the time required. An approximate idea of the unsaturation may, therefore, be obtained by comparison with standard oils of known iodine value. A preliminary determination of unsaturation in this qualitative manner, will be found useful for the accurate determination of the iodine value by standard methods as the quantity of the oil to be taken for iodine value determinations is dependent on the unsaturation and hence the previous knowledge of approximate unsaturation would be of great help.

(c) *Identification of Individual Oils in a Mixture.*—It has already been observed that when an oil is treated with pyridine and potassium permanganate, two characteristics are brought out, *viz.*, (1) temperature of carbon dioxide evolution, and (2) the quantity of carbon dioxide evolved. The former serves to detect the component oils of a mixture of the temperature of carbon dioxide evolution of an oil is not influenced by the presence of other oils, so that an oil having a lower temperature of carbon dioxide evolution behaves as if other oils were absent. When the heating is conducted slowly, the evolution of carbon dioxide for any particular oil begins at a constant temperature and if the oil is maintained at or near about that temperature, the evolution of carbon dioxide is quite exhausted after a time and no further evolution takes place on raising the temperature. This complete evolution of carbon dioxide within a narrow range (usually 5°) makes it possible to detect and estimate different oils in a mixture with the help of the characteristics referred toabove.

It is, however, to be noted that the presence of free acids lower the temperature of carbon dioxide evolution while the quantity of carbon dioxide is increased. It is, therefore, necessary to know the acid value of an oil along with the carbon dioxide constants. These constants of different oils are shown in the following table with their respective acid values.

The carbon dioxide value may be defined as the amount of carbon dioxide in grams evolved per 100 grams of oil.

TABLE I.

The Carbonic Acid Constants for Different Oils.

Name of oil.	Acid value (in oleic acid %)	Temp. of CO_2 evolution.	Oil taken in g.	CO_2 evolution in g.	CO_2 value.	Mean.
Ghee (1)	0·082	85	—	—	—	—
Ghee (2)	0·063	85	—	—	—	—
Cocoanut oil (1)	1·95	75	1·6336 2·0294	0·01394 0·01768	0·8532 0·8714	0·8623
Cocoanut oil (2)	2·02	75	1·2340 1·4652	0·01112 0·01354	0·9036 0·9214	0·9125
Cocoanut oil (3)	2·01	75	0·8932 1·5636	0·00544 0·01468	0·9229 0·9391	0·9310
Mohua oil	33·75	68	0·6942 1·1128	0·05040 0·06341	5·6390 5·6281	5·6310
Castor oil	2·15	80	2·1236 1·3206	0·01000 0·00627	0·4706 0·4746	0·4726
Sesame oil	0·34	65	2·4632 1·5694	0·00852 0·00549	0·3462 0·3500	0·3481
Groundnut oil (1)	5·62	65	2·7240 1·2944	0·07444 0·03512	2·7332 2·7154	2·7240
Groundnut oil (2)	5·46	65	1·8942 1·0464	0·05166 0·02834	2·7284 2·7080	2·7182
Mustard oil	7·25	69	2·3204 1·6536	0·02396 0·01602	1·0329 0·9691	1·0010
Chaulmoogra oil	14·65	50	1·8924 1·3262	0·03008 0·02191	1·5899 1·6532	1·6215
Olive oil	4·32	70	2·2234 1·9864	0·03178 0·02758	1·4330 1·3887	1·4010
Cotton seed oil	28·115	60	1·2460 1·3642	0·03750 0·04051	3·0102 2·9728	2·9915
Linseed oil	1·38	80	0·9944 2·0254	0·01482 0·03112	1·5698 1·5374	1·5536
Tallow (mutton)	3·01	80	1·2446 1·8324	0·01506 0·02290	1·2130 1·2470	1·2300
Codliver oil (Medicinal "De Jons")	0·12	62	1·4322 1·8696	0·01006 0·01305	0·7029 0·7213	0·7121
Fish oil (Rohita)	0·44	60	2·2234 1·9864	0·05036 0·04522	2·2632 2·2766	2·6299
Hydrogenated oil ("vegetable product—Denmark")	8·32	85	—	—	—	—
Lanoline	—	85	—	—	—	—

It will be evident from the data that for the same oil from different sources, both the temperature of carbon dioxide evolution and carbon dioxide value remains constant within the limits of experimental error, provided the acid value of the oil does not vary to a great extent. As has already been indicated, these constants may be utilised for the detection and estimation of adulterations in commercial fats. The usual procedure would be to remove any free acids occurring in the fat to be tested and then to subject it to the oxidising action of dry potassium permanganate in the presence of pyridine, the temperature being raised very gradually up to 85°. The lowest temperature at which carbon dioxide first appears and makes the baryta turbid, is carefully noted and the temperature maintained near about this point for some 45 minutes. When the carbon dioxide evolution is exhausted, the temperature is again raised slowly, subsequent temperatures of carbon dioxide evolution are noted and the procedure repeated. The amount of carbon dioxide evolved at each temperature is carefully determined in the usual manner. The values thus obtained lead to the detection and approximate determination of adulteration. It will be evident from the experimental portion that quite a number of artificial mixtures made in the laboratory were tested in this way, both qualitatively and quantitatively (special emphasis being given to the adulterations in ghee) and the results were found to be satisfactory. A few unknown samples were also tested with satisfactory results.

(*d*) *Quantitative Estimation of Oils.*—The application of carbon dioxide value for quantitative estimations of oils is particularly interesting as at present there are no methods available for the direct estimation of oils in a mixture. If the mixture consists of two known oils and the iodine values of the two components are also known, the constituents may be estimated from the iodine value of mixture. But this method fails completely when the mixture contains more than two oils or the identity and the iodine values of the constituents of the mixture are not known. In such cases, the new carbonic acid constants may be applied with satisfactory results. It, must, however, be remembered that quantitative estimation of oils can only be approximate, as the characteristics of an oil vary to a certain extent according to the source from which it is derived as well as the conditions such as soil, diet, climate, etc., under which it is formed. From the table it will be evident that

carbon dioxide values of purified oils from different sources do not vary to a great extent and hence these may be utilised to get a rough idea of the quantities of oils present in a mixture. It has, however, to be admitted that a sufficiently large number of tests with oils from widely different sources have not yet been completed.

When the temperature of carbon dioxide evolution of the constituent oils in a mixture differs by more than 10° the oils may be estimated directly from their carbon dioxide values, whatever be the number of constituents in the mixture. But when the difference is less than 10° the estimations are not sufficiently accurate as small amount of carbon dioxide emanating from an oil of higher temperature of carbon dioxide evolution contaminates the carbon dioxide value obtained at a lower temperature, though the total carbon dioxide remains unchanged. In such cases, the constituents should first be detected from the temperature of carbon dioxide evolution and when the mixture consists of two oils only, the percentage constituent oils may be determined from the carbon dioxide value of the mixture as well as those of individual oils. Still a preliminary determination of the oil having the lowest temperature of carbon dioxide evolution in the usual manner would often be found of great help ("preliminary experiment"), when it has been found that the result thus obtained is somewhat (within 8%) greater than the actual value.

When the mixture consists of three oils, whose temperatures of carbon dioxide evolution are widely different, the percentages of the constituents may be determined directly from the carbon dioxide values. In cases where the above condition is not satisfied but the constituent oils are known, the percentages may be determined from the following 3 equations, there being only 3 unknown factors:—

$$X+Y+Z=100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

$$X.C+Y.C'+Z.C''=100C''' \quad \ldots\text{(ii)}$$

$$X.I+Y.I'+Z.I''=100I''' \quad \ldots\text{(iii)}$$

where X, Y, Z are the percentages of the 3 respective oils, C, C', C'' and I, I', I'' are their respective carbon dioxide and iodine values. C''' and I''' are respectively the carbon dioxide and iodine values of the mixture.

EXPERIMENTAL.

The oils and fats used in these experiments were obtained from market and were free from adulterations. These were kept in the dark and filtered before use. Oils from different sources used in these experiments are indicated by different numbers of samples. The chemicals used were extra pure Merck's reagents. In the case of pyridine, it was further purified by distillation in the laboratory.

Procedure.—1—2 G. of oil dissolved in 50 c.c. of pyridine was taken in a round-bottomed flask and an admixture of finely powdered dry potassium permanganate (0·2 to 0·4 g.) and anhydrous magnesium sulphate was added, the latter being intended to neutralise any potassium hydroxide formed during oxidation which might otherwise cause saponification of the fat. The flask was shaken for about two minutes and fitted to a reflux condenser, the upper end of which was connected to the absorption vessels containing decinormal baryta. Air freed from carbon dioxide was led into the bottom of the flask by means of a glass tube perforated at the end. This served to stir the contents as well as to drive out any initial carbon dioxide in the flask. The temperature was then raised by heating the flask in an oil bath. The carbon dioxide was estimated by means of decinormal baryta water (200 c.c.) contained in 2 conical flasks connected in series. The heating was made at the rate of 2° per minute and air was passed at the rate of about 80 bubbles per minute.

The temperature at which baryta water first turned milky was taken as the minimum temperature of carbon dioxide evolution and this temperature was kept constant for about one hour to ensure complete exhaustion of carbon dioxide, which was tested by holding a few drops of lime water at exit. Heating was then continued to a higher temperature and any subsequent evolution of carbon dioxide was observed in the same manner. The estimation of carbon dioxide made by allowing the precipitate in the baryta to settle when a measured amount of superincumbent liquid was drawn out and titrated with decinormal hydrochloric acid.

Precautions.—(1) Care should be taken that pyridine vapour might not find its way into the baryta water. For this reason, the

rate of passing air should not be too great and a long condenser should be used.

(2) In case the contents of the flask become semi-solid, as in the case with drying and semi-drying oils, these will become fluid again on warming.

Blank experiment indicated that pyridine is quite stable under the above conditions. No trace of carbon dioxide could be detected on maintaining a temperature of 85° for 40 minutes and only 0·0022 per cent. was evolved on raising the temperature to 100° in the course of some 20 minutes. As most oils and fats evolve carbon dioxide below 85° pyridine may be considered quite an inert solvent having no influence on the carbon dioxide value of the oil. The temperatures of carbon dioxide evolution and the carbon dioxide values of different individual oils have already been given in Table I.

Detection and Estimations of Oils in a Mixture Containing two or more Constituents.—The two characteristics mentioned above have been taken advantage of in identifying and estimating oils in a mixture of 2 or 3 components. As has already been pointed out, the temperature of carbon dioxide evolution serves to identify the oils while the carbon dioxide value is of great importance in estimating the oils. When the difference of temperatures of carbon dioxide evolution is more than 10°, the oils are estimated directly and in other cases recourse has to be taken to the formulae already indicated in the theoretical section. No satisfactory results can be obtained with a mixture of ghee and hydrogenated oil as in both cases evolution of carbon dioxide took place above 85°. Results obtained with different mixtures are given in Table II.

The mixtures examined in this work have been chosen arbitrarily but they are sufficiently wide to indicate the range of applicability of this test. Thus commercially important mixtures such as mustard and groundnut oils, though not examined in this paper, should evidently behave as a mixture of mustard and olive oils will do. As oils from widely different sources have not been examined, it cannot be claimed that figures given in this paper will be found accurate in all cases. The constants should be determined independently in these cases where absolutely reliable information on mixtures of oils from different sources is wanted.

TABLE II.

Mixture.	Percentage composition of mixture.	Quantity taken.	Permanganate used.	Temp. of CO_2 evolution.	CO_2 value of mixture.	CO_2 value of 1st component.	CO_2 value of 2nd component.	Percentages found.
Ghee and cotton seed oil.	58·4 41·6	4·6782g.	0·467g.	60°	1·4205	—	2·9915	58·2 41·8
Do.	50·6 49·4	1·6996	0·17	60°	1·5402	—	2·9915	48·6 51·4
Ghee and mahua oil.	50·03 49·97	2·4694	0·25	68°	2·7530	—	5·6310	51·2 48·8
Do.	78·1 21·9	2·5454	0·254	68°	1·1805	—	5·6310	79·92 20·08
Ghee and cocoanut oil.	29·3 70·7	2·7996	0·28	75°	0·6852	—	0·9019	24·1 75·9
Do.	52·28 47·72	1·9726	0·197	75°	0·4419	—	0·9019	50·95 49·05
Ghee and olive oil.	65·17 34·83	3·5612	0·355	70°	0·4897	—	1·401 0	65·1 34·9
Do.	30·29 69·71	2·8527	0·285	70°	0·9784	—	1·401	30·2 69·8
Ghee and mutton tallow.	47·38 52·62	2·0318	0·202	80°	0·6866	—	1·2801	44·2 55·8
Do.	68·3 31·7	2·6646	0·266	80°	0·892	—	1·2801	68·1 31·9
Olive oil and groundnut oil.	50·7 49·3	2·7352	0·273	65°	2·0722	1·4010	2·7286	52·4 47·6

TABLE II—(*Contd.*).

Mixture.	Percentage composition of mixture.	Quantity taken.	Permanganate used.	Temp. of CO_2 evolution.	CO_2 value of mixture.	CO_2 value of 1st. component.	CO_2 value of 2nd component.	Percentages found.
Olive oil and groundnut oil.	31·8 68·2	3·8794g.	0·388g.	65°	2·2927	1·4010	2·7286	32·89 67·11
Olive oil and sesame oil.	32·3 67·7	1·8196	0·183	65°	0·6704	1·4010	0·348	31·4 68·6
Olive oil and cocoanut oil.	59·2 40·8	4·5060	0·45	70°	1·1611	1·4010	0·9019	53·8 46·2
Olive oil and cotton seed oil.	65·5 34·5	2·3850	0·238	60°	1·0188 (60°)	—	2·9915	65·92 34·08

CHEMICAL LABORATORY,
DACCA UNIVERSITY

Received May 4, 1931.

On Activated Charcoal. Part I.

By Satyaprasad Roychoudhury.

The activation of charcoal has been ascribed to a variety of possible causes, *e.g.*, broadening of the pores, change in the structure of the surface layer, breakdown of the crystal structure (Philip, *J. Chem. Soc.*, 1920, **117**, 361; Ogawa, *Biochem. Z.*, 1925, **161**, 275; *ibid.*, 1926, **172**, 249; Freundlich, Capillary Chemistry, Eng. Ed., 1926, p. 183; Kolthoff, *Rec. trav. chim.*, 1929, **48**, 549; Ruff and Mautner, *Koll.-Chem. Beih.*, 1928, **26**, 549). The optimum conditions have not however been correlated with any definite property of the charcoal. In fact Dubinin has observed (*Z. Phys. Chem.*, 1929, **140**, 81) that the order of adsorption of aliphatic acids changes with the conditions of activation. Thus the optimum condition would vary with the nature of the adsorbate (see also Ogawa *loc. cit.*). The role of substances other than carbon which may be formed during activation or may be present as impurities has recently received prominent attention. Miller (*J. Phys. Chem.*, 1926, **30**, 1031) prepared ash-free sugar charcoal and attributed the different observations of Michaelis and Rona (*Biochem. Z.*, 1919, **97**, 57; *ibid.*, 1919, **94**, 240) to the inorganic constituents of the ash present in their sample.

The recent works of Schilow and his co-workers (*Z. Phys. Chem.*, 1928, **138**, 188; *ibid.*, 1928, **136**, 84; *ibid.*, 1929, **143**, 41; *ibid.*, 1930, **148**, 233; *ibid.*, 1930, **149**, 211; *ibid.*, 1930, **150**, 31; *Kolloid Z.*, 1930, **52**, 107) and of Frumkin and his co-workers (*Z. anorg. Chem.*, 1926, **158**, 84; *Z. Phys. Chem.*, 1929, **141**, 141, 290; *ibid.*, 1930, **147**, 125; *ibid.*, 1930, **150**, 421; *ibid.*, 1930, **151**, 87; *Kolloid Z.*, 1930, **51**, 128) constitute a fundamental advance both in the technique and in the knowledge of the subject. Schilow and his co-workers emphasise the role played by oxides of carbon formed during activation. Schilow assumes the formation of two basic oxides A and B and an acidic oxide C whose stability depends on the temperature.

In explaining the different orders of adsorption Schilow and co-workers have shown that activated charcoals can be prepared from pure sugar which adsorbs (*i*) only an acid (hydrochloric) but not an alkali (sodium hydroxide), (*ii*) only an alkali but no acid, (*iii*) both the acid and the alkali. These results are difficult to reconcile with the theory of Frumkin (see later), according to which charcoal prepared under these conditions should function as an oxygen electrode and should adsorb acids but not alkalies. The observations of Kruyt and Kadt (*Kolloid Z.*, 1929, **47**, 44) who found that sugar charcoal activated in oxygen had a negative charge and that this sample adsorbed alkali are also against Frumkin's theory as these samples should have a positive charge and adsorb no alkali.

Frumkin explains them by assuming that these samples contain acid substances formed by activation. Kruyt and Kadt (*loc. cit.*) also found that charcoal activated in carbon dioxide had a positive charge and did not adsorb alkali. This shows that the charcoal does not always behave as an oxygen electrode in Frumkin's sense. In explaining the different orders of adsorption of aliphatic acids with the conditions of activation of charcoal observed, Dubinin (*Z. Phys. Chem.*, 1930, **150**, 145, 154) considers that the size of the pores and the effective surface have to be considered in addition to the presence of such oxides. These observations are also difficult to account for on the basis of Frumkin's theory (see later). The explanation of adsorptive properties of charcoal upheld by Frumkin and his co-workers (*loc. cit.*) is very simple and attractive and rests on classical electrochemical considerations. Charcoal functions as an oxygen or hydrogen electrode in the presence of the respective gases analogous to the wellknown behaviour of platinum. There would thus exist the well known relation between the pressure of oxygen or hydrogen and the acid or alkali adsorption respectively. Frumkin in a series of fine experiments has shown that treatment with oxygen increases and treatment with hydrogen decreases the adsorption of acids—this is in qualitative agreement with his theory. Both Schilow and Frumkin however agree that the simple quantitative relationship between the adsorbed amounts of acid or alkali and amounts of gaseous oxygen and hydrogen respectively consumed during this process is not satisfied. Changes in the composition and chemical nature of the oxides postulated by Schilow or of other substances with similar properties if present in the charcoal surface would account for the qualitative agreement. On

account of the fact that charcoal when activated even in presence of hydrogen absorbs acids, Frumkin holds that the hydrogen charcoal is difficult to prepare and charcoal free from platinum behaves always as an oxygen charcoal. This is attributed to the great affinity of charcoal for oxygen. That complex oxides, as suggested by Schilow, may be present is not denied by Frumkin (*Kolloid Z.*, 1930, **51**, 126) but it is held that the mechanism of acid adsorption is that stated above. In analogy with the wellknown case of the platinum-oxygen electrode, oxygen charcoal is assumed to have a positive charge resulting from the displacement of an electron from the surface. The hydroxyl ions formed from the union of the negatively charged oxygen ions and a molecule of water leave the surface and neutralise the hydrogen ions so that the anion (*e.g.*, chloridion of hydrochloric acid) would form a sort of chloride of carbon. Similarly charcoal containing a small percentage of platinum, which Frumkin holds acts as a hydrogen electrode in presence of hydrogen, would have a negative charge, neutralise alkali and form a 'sodium-carbon' electrolyte. The amounts of acid or alkali adsorption measure respectively the amount of oxygen or hydrogen consumed during the adsorption process. Frumkin (*Z. Phys. Chem.*, 1930, **147**, 145) in fact suggests that what matters is the thermodynamic potential of the oxygen in the charcoal electrode and it is immaterial in what form the oxygen is present in the charcoal. The exact function of the oxygen is however most important for a corrrect understanding of the mechanism of the reaction and also in deciding the correctness or otherwise of Frumkin's theory. Schilow has shown and Frumkin agrees that the curve of adsorption of acid by *outgassed* charcoal at various oxygen pressures shows a form contrary to the exponential relation postulated in this theory. Frumkin points out that the evidence leads to a saturation oxygen potential (*Z. Phys. Chem.*, 1930, **150**, 432). Further, on exhausting charcoal of gases at high temperature and vacuum and then introducing air. it is found that the adsorption of valerianic acid increases but the power to adsorb hydrochloric acid diminishes (*Z. Phys. Chem.*, 1930, **150**, 43) which is also difficult to account for from this theory. For the picture would be different according as an oxide of carbon regulates the hydroxyl-ion concentration (as for example is the case with say, mercury-mercuric oxide electrode) or the pressure of oxygen determines it. A mercury-mercurous oxide electrode would act as a hydroxyl-ion electrode even in the complete absence of oxygen (*e.g.* in nitrogen), whereas if no simiiar stable oxide of carbon were present, charcoal should

absorb no acid in the complete absence of gaseous oxygen. Frumkin (*Z. Phys. Chem.*, 1930, **150**, 435) finds however that even platinum charcoal in presence of hydrogen, which he concludes from other experiments (*Kolloid Z.*, 1930, **51**, 123) behaves as a hydrogen electrode, adsorbs acids but should not do so. He explains this by assuming that an additional loose type of adsorption similar to that in an air-water interface (*i.e.* the well known Gibb's type of adsorption) manifests itself at high concentrations. There is also a negative adsorption of acids by the same charcoal at low concentration. This he refers to the adsorption of water by the charged charcoal surface. Still another type of absorption is assumed by Frumkin in addition to the above for he (*Z. Phys. Chem.*, 1929, **141**, 150) finds that the adsorption of benzoic acid is the same for oxygen charcoal and hydrogen charcoal containing ·2% platinum. This is remarkable as this cannot be reconciled with Frumkin's simple theory. Frumkin further points out in the first paper of the series (*Z. Phys. Chem.*, 1929, **141**, 144) that his theory does not apply to the observations of Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 191 ; also Mukherjee and Basu, *ibid.*, 1926, **3**, 371) and of Ghosh (*J. Chem. Soc.*, 1926, p. 2605) on hydrolytic adsorption by silicic acid, manganese oxide and other substances. This is important and shows that if definite acidic or basic oxides exist on the charcoal, they are sufficient in themselves to account for the observations. As indicated above, an insoluble film of basic oxide would act as a reversible oxygen (hydroxyl ion) electrode. There is no question of oxygen consumption or presure of oxygen in such an equilibrium, unless the composition of the oxide varies with oxygen pressure.

Both Frumkin and Schilow have tried to correlate the electric charge of the charcoal surface with its behaviour in such adsorptive processes. In opposition to Frumkin, Schilow holds that charcoal is a negative absorbent and has a strong (preferential) adsorption of anions. It should thus be charged negatively in water as also in neutral electrolytes and the adsorption of the acid is attributed to the covering up of the anions by hydrogen ions, displaced from the solution by what he terms *'molarisation'* as also through the existence of an adsorption potential of cations, analogous to the electrochemical potential series. The more positive element is supposed to displace hydrogen ions from the solution to the interface. It will be seen later that the charcoal

does not act as a negative adsorbent in Schilow's sense. To account for non-adsorption or negative adsorption of alkali, Schilow assumes that (*Z. Phys. Chem.*, 1928, **138**, 188) "hydroxyl ions are adsorbed out of water and out of alkali" and they *in turn* adsorb hydrogen ions but not alkali metal cations and a molecular adsorption occurs. With activated charcoal, however, the more it is washed with water, the more it assumes a positive charge. Further, it will be seen that there is a relationship between the charge of the surface and the adsorption of acid or alkali not contemplated in Schilow's theory. Schilow's own observation that charcoal can adsorb both acid and alkali definitely contradicts his assumption that charcoal primarily absorbs hydroxyl ions and hydrogen ions only through molarisation or displacement from solution by the more positive cation. *Neither Schilow nor Frumkin has however made experiments on the charge of the charcoal surface.*

That absorption of ions, hydrolytic adsorption and adsorption of electrolytes are closely correlated with the electrical charge has been shown by Mukherjee and co-workers (*Phil. Mag.*, 1922, **44**, 321; *J. Indian Chem. Soc.*, 1925, **2**, 219 ; also, *Proceedings, Indian Science Congress*, 1929, p. 93 ; *Kolloid Z.*, 1929, **49**, 362). A theory similar in some respects to that of Mukherjee was later suggested also by Bartell and Miller (*J. Phys. Chem.*, 1924, **28**, 992) to account for hydrolytic adsorption by charcoal. The electric charge of the charcoal surface is also of interest in relation to the work of Fromageot (*Compt. rend.*, 1924, **179**, 972, 1404; Nature, Sept. 14, 1929) who states that charcoal adsorbs neutral molecules of acids and not ions. Phelps and Peters (*Proc. Roy. Soc.*, 1929, A **124**, 554) are also of the same opinion. Umetsu (*Biochem. Z.*, 1928, **135**, 442) found that acids and alkalies have a marked effect on the electrical charge of the surface.

The exact function of substances other than carbon thus constitutes a very important point at issue.* The work of Pawlow (*Kolloid Z.*, 1924, **35**, 225) is of interest in that it indicates how the presence of substances can be verified by determining the effect of mass on the adsorption. The present paper deals with (A) condition of maximum activation; (B) the effect of mass of the absorbent; (C) purifica-

* Bhatnagar, Mathur and Kapur (*Indian J. Phys.*, 1927-28, **3**, 59) hold from measurements of the magnetic susceptibility of charcoal with $Fe^{...}$ ions adsorbed on it that chemical changes of the type postulated by Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361) take place between the adsorbent and the adsorbed material.

tion of activated charcoal by washing; (D) order of adsorption of acids; (E) equivalent adsorption of ions of an acid; (F) effect of ethyl alcohol on the adsorption of acids by different samples of charcoal; (G) hydrolytic adsorption and electrical charge on the charcoal surface.

Preparation of Materials.

(1) *Animal Charcoal.*—Merck's animal charcoal was finely powdered and digested with hydrochloric and hydrofluoric acids in a platinum basin. It was next washed several times with boiling conductivity water (Miller, *J. Phys. Chem.*, 1926, 30, 1031). The electrical conductivity of the wash liquid (boiling conductivity water) offers the best test of removal of electrolytes. After boiling 15 g. of charcoal with 500 c.c. of conductivity water 20 times, the specific conductivity fell from $\cdot 156 \times 10^{-5}$ to $\cdot 173 \times 10^{-5}$ r. o. These purified samples were used for activation in an electric furnace. A closed silica tube, with a tight rubber cork fitted with glass tubes connecting with a Cenco vacuum pump and a pressure gauge, was used. After activation, the charcoal was cooled and transferred into clean stoppered Jena glass bottles. Exposure to the atmosphere was as brief as possible. The bottles were kept inside a big vacuum desiccator containing caustic soda sticks and phosphorus pentoxide. Two perforated zinc sheets were placed horizontally at some distance from each other above the desiccating agents.

(2) *Sugar Charcoal.*—Merck's extra-pure cane sugar was used and the charcoal prepared as given by Miller (*loc. cit.*). The charcoal was boiled several times with conductivity water before activation (samples J to Q).

(3) *Gelatin Charcoal.*—Merck's ordinary pure gelatin was ignited strongly in a covered silica basin in order to burn off tarry matter. It was then powdered and again ignited free from the combustible ingredients. It was purified, activated and preserved as above (samples R and S).

A. *Conditions of Maximum Activation.*

The extent of activation of animal, sugar and gelatin charcoals prepared under different conditions of temperature, duration of heating, and in contact with air (10 mm. pressure), as also in contact with dry and well-purified N_2 and CO_2 (in the case of animal and

sugar charcoal only) has been measured from the adsorption of benzoic acid (0·02 *N*) (Miller, *loc. cit.*). 50 C.c. of the electrolyte were kept in contact with the charcoal for 20 hrs. The upper liquid was separated by means of a powerful centrifuge. Baryta and phenolphthalein were used for titration.

Changes in volume due to the admixture and the adsorption of the solvent are negligible. The amounts adsorbed are given below in gram moles per gram of charcoal multiplied *thousand* times and the amount of charcoal in grams. The concentrations are in normality.

TABLE I.

Animal charcoal : activated with air : pressure-10 mm.

Sample.	Temp. (°C.).	Duration (hrs.).	Amount (g.).	Initial conc. (*N*).	Final conc. (*N*).	Amount adsorbed (*g. mole/g.* $\times 10^3$).
A	700°	4	·125	·021	·0146	2·56
			·25	·021	·01	2·2
			·5	·0196	·0021	1·75
B	600°	4	·125	·021	·0154	2·24
			·25	·021	·01	2·2
			·5	·0196	·0032	1·64
C	600°	8	·125	·021	·0142	2·72
			·25	·021	·0084	2·52
			·5	·0196	·0015	1·81
D	600°	28	·125	·0208	·0146	2·48
			·25	·0208	·0102	2·12
			·5	·0196	·0020	1·76

TABLE II.

Animal charcoal : activated with carbon dioxide : atmospheric pressure.

Sample.	Temp. (°C.)	Duration (hrs.).	Amount (g.).	Initial conc. (*N*).	Final conc. (*N*).	Amount adsorbed (*g. mole/g.* $\times 10^3$).
E	600°	4	·125	·0208	·0142	2·64
			·25	·0208	·0081	2·54
			·5	·0196	·0017	1·79
F	600°	8	·125	·0208	·0144	2·56
			·25	·0208	·009	2·36
			·5	·0196	·0022	1·74
G	600°	28	·125	·0208	·0141	2·68
			·25	·0208	·0084	2·48
			·5	·0196	·0015	1·81

TABLE III.

Animal charcoal : activated with nitrogen : atmospheric pressure.

Sample.	Temp. (°C.).	Duration (hrs.).	Amount (g.).	Initial conc. (*N*).	Final conc. (*N*).	Amount adsorbed ($g./mole \times 10^3$).
H	600°	4	·125	·0208	·0157	2·04
			·25	·0208	·0104	2·08
			·5	·0196	·0039	1·57
I	600°	24	·125	·0198	·0151	1·88
			·25	·0198	·0097	2·02
			·5	·196	·004	1·56

TABLE IV.

Sugar charcoal : activated with air : pressure 10 mm.

Sample.	Temp. (°C).	Duration. (hrs.).	Amount. (g.).	Initial conc. (*N*).	Final conc. (*N*).	Amount adsorbed ($g./mole/g \times 10^3$).
J	900°	4	·125	·0208	·0191	·68
			·25	·0208	·0186	·44
			·5	·0208	·0175	·33
K	900°	8	·125	·0196	·0196	0
			·25	·0196	·0191	·1
			·5	·0196	·0177	·19
L	900°	24	·125	·0196	·0196	0
			·25	·0196	·0193	·06
			·5	·0196	·0179	·17
M	600°	4	·125	—	—	—
			·25	·0196	·0187	·18
			·5	·0196	·0168	·28
N	600°	8	·125	·0196	·0192	·16
			·25	·0196	·0186	·2
			·5	·0196	·0173	·23

TABLE V.

Sugar charcoal: activated with carbon dioxide: atmospheric pressure.

Sample.	Temp. (°C).	Duration. (hrs.).	Amount. (g.).	Initial conc. (*N*).	Final conc. (*N*).	Amount adsorbed. (*g. mole/g.* $\times 10^3$).
O	900°	4	·125	·0196	·0186	·4
			·25	·0196	·0178	·36
			·5	·0196	·016	·36
P	900°	8	·125	·0196	·0187	·36
			·25	·0196	·0184	·24
			·5	·0196	·0168	·28
Q	900°	24	·125	·0196	·0196	0
			·25	·0196	·0193	·06
			·5	·0196	·0187	·09

TABLE VI.

Gelatin charcoal: activated with air: pressure 10 mm.

Sample.	Temp. (°C).	Duration. (hrs.).	Amount. (g.).	Initial conc. (*N*).	Final conc. (*N*).	Amount adsorbed (*g mole/g.* $\times 10^3$).
R	600°	4	·125	·0198	·0182	·64
			·25	·0198	·0186	1·24
			.5	·0196	·0184	·12
S	600°	28	·125	·0198	·0188	·40
			·25	·0198	·0173	·50
			·5	·0196	·0183	·13

An increase in the time of activation at first seems to produce an increase in adsorptive power but if the time is longer a decrease results (B and C; F and G; C and D). On the other hand, samples H to S show a uniform decrease in the adsorptive power. This lowering is most marked with sugar charcoal, which acquires a distinctly granular form after activation.

An increase in temperature, the time being kept constant, does not produce a uniform effect. In two cases, *viz.*, with samples A & B and J & M, an increase of temperature causes

an increase in the adsorptive power considerably. K and N however show a decrease in activation with an increase of temperature, the duration of heating being kept at 8 hrs. in this case. Probably in such cases graphitisation sets in.

The indications are that the optimum condition depends on the sample. A higher temperature in some cases compensates for a shorter interval of activation. Carbon dioxide produces on the whole a greater activity. Animal charcoal is decidedly the best adsorbent for the acid. Nitrogen gas appears to have an adverse effect on the adsorptive power of animal charcoal. In Table VII, the order of adsorptive power (decreasing) is given. It will be seen that it depends on the amount of charcoal though the same amount of acid is taken.

TABLE VII.

Amount of Charcoal (g.).	Order of adsorbability.
·125	C>G>E>A>F>D>B>H>I>J>R>S, O>P>N>K, L, Q.
·25	E>C>G>F>A, B>D>H>I>R>S>J>O>P>N>M>K>L, Q.
·5	C, G>E>D>A>F>B>H>I>O>J>M, P>N>L>S>R>Q.

B. *The Anomalous Effect of the Mass of Adsorbent.*

If there be an equilibrium distribution of a solute between the surface of an adsorbent and the solution, the fundamental condition should be satisfied that the amount of adsorption would be a definite function of the activity of the solute in the solution. If the extent of surface per unit mass and the nature of the surface does not change with change of concentration of the solute or there be no substance present on the surface which can distribute itself between the liquid and the interface, then the amount of solute in the surface and that in the solution would vary directly, provided that we are dealing with *positive* adsorption, As the *end concentration* decreases, the amount adsorbed per unit mass should also decrease. Our results show that this condition is not satisfied in several instances and that foreign substances, are present which partake in the distribution between the interface and the solution and also react with the acid. A lower *end concentration* of solute (*cf.* Samples K to N, P to S) produces

greater adsorption per unit mass, when the total mass of the adsorbent increases. Sugar charcoal shows the greatest discrepancy in this respect. Further, this charcoal frequently shows no adsorption, when a small amount (0·125 g.) is taken (K, L, M, Q).

The possible presence of foreign substances is of great interest in view of the contradictory results recorded in the literature. On the assumption that substances which can chemically react with the acid are present and that such reactions (*e.g.*, neutralisation or exchange adsorption) proceed to completion, the amount adsorbed *per unit mass*, calculated as above, should be constant and independent of the end concentration. The results cannot thus be accounted for by such assumptions. It is possible that the surface contains both acidic and basic substances, not necessarily as neutral salts, and that this is responsible for the observed effect of the mass of the charcoal. This calculation is borne out by subsequent observations. It is hoped to deal with this increased adsorption at lower concentration of benzoic acid more in detail in a later communication.

C. *Purification of Activated Charcoal by Washing.*

The importance of the electric charge of the charcoal surface has been indicated in the introduction. The removal of impurities by washing has been followed from conductivity measurements and the resulting changes in the electric charge of the surface has been noted.

Animal Charcoal : The charcoals used in the experiments under this section were all *activated at* 600° *for* 6 *hrs., at a reduced pressure of* 10 *mm. of air.*

Animal charcoal was purified and boiled with conductivity water 8 times. On activation, the resulting charcoal was found to have a negative charge (ash-content·15 per cent.). As previous workers do not record purification of the samples after activation, these were repeatedly boiled with conductivity water. A fall in conductivity, indicating gradual purification, was noticed. After four days, during which the sample was digested 20 times, the animal charcoal was still found to set free detectable amounts of electrolytes. The specific conductivity of the water rose from $\cdot 78 \times 10^{-5}$ to $1 \cdot 56 \times 10^{-5}$ r. o. on being kept in contact with the sample thus obtained.

As a result of this washing the sign of the charge of the charcoal was reversed from negative to positive. The cataphoretic

speeds* (*vide*, Mukherjee, *Proc. Roy. Soc.*, 1923, **A 103**, 102) were respectively -117×10^{-5} and $+20 \times 10^{-5}$ cm./sec., under unit potential gradient. The sign indicates the charge of the solid surface. The particles had a considerable velocity of fall and the average of upward and downward movements was taken.

Sugar Charcoal: The charge of sugar charcoal at successive stages of purification was measured by the electro-osmotic method. The finer particles show cataphoresis and this interferes with the accuracy. 15 G. of charcoal were shaken with 500 c. c. conductivity water.

TABLE VIII

Sugar Charcoal.

Name of sample.	I	II	III	IV	V
Sp. conductivity of supernatant liquid (r. o.)	$2{\cdot}4 \times 10^{-6}$	$\cdot74 \times 10^{-6}$	$\cdot65 \times 10^{-6}$	$\cdot65 \times 10^{-6}$	$\cdot65 \times 10^{-6}$
Electro-osmotic movement of the bubble in cm. per 8 minutes :	$-\cdot2$	$-\cdot5$	$-1{\cdot}45$	$+\cdot25$	$+\cdot9$

Samples I and II were digested with a limited amount of hot water before activation. They have a negative charge. The conductivity of the supernatant liquid is higher than in the other instances. On further activation of II at 600° (2 hrs.) III was obtained. It shows a lower conductivity but a greater osmosis. The latter observation does not mean a greater negative charge as the size of the particles have to be considered. IV was prepared from III by further digestion and subsequent activation (600°, 6 hrs.). The conductivity of the wash-water for this sample has the same value as in III but the sign of the charge becomes reversed. On further washing this sample, the resulting charcoal V shows a constant conductivity but a greater positive charge. These results show that both on digestion and on activation, the charcoal tends to have a positive charge.

* The suspension remains stable for three hours.

Further experiments on the effect of purification: The following electro-osmotic measurements were carried out at room temperature with charcoal, which was not washed after activation. It has been observed that activation itself results in the partial removal of the electrolytic foreign substances.

TABLE IX.

Sample.	Movement of bubble : (cm. in 3 min.).
Merck's original blood charcoal	− ·8
Ditto purified as above but not activated.	+ ·14
Ditto purified and activated.	+ ·24
Merck's original active carbon.	−1·69
Ditto purified and activated.	+ ·8
Sugar charcoal impure (obtained by ignition of cane sugar).	−4·3
Ditto purified and activated.	+1·5
Ditto purified and activated (obtained by dehydration of cane sugar with H_2SO_4).	+2·07
Merck's original animal charcoal.	+1·9
Ditto purified and activated.	+1 1
Gelatin charcoal impure.	−13·0
Ditto purified and activated.	+ ·2

In all these instances, on purification or activation, the charcoal acquires a positive charge. This observation is most interesting in view of the statement by Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 219) that "their * charcoal would probably show a positive charge in contact with pure water." It has been stated that the views of Bartell and Miller (*J. Phys. Chem.*, 1924, **28**, 992) on hydrolytic adsorption by charcoal are similar to those of Mukherjee (*Phil. Mag.*, 1922, **44**, 321; also *loc. cit.*). Kolthoff (*loc. cit.*) points out that there is an essential difference in detail between the two hypotheses. From Mukherjee's point of view the positive charge of sugar charcoal in contact with water indicates either (*i*) a preferential primary adsorption of hydrogen ions as compared to hydroxyl ions or (*ii*) the presence of the cation of a basic oxide on the charcoal

* Bartell and Miller,

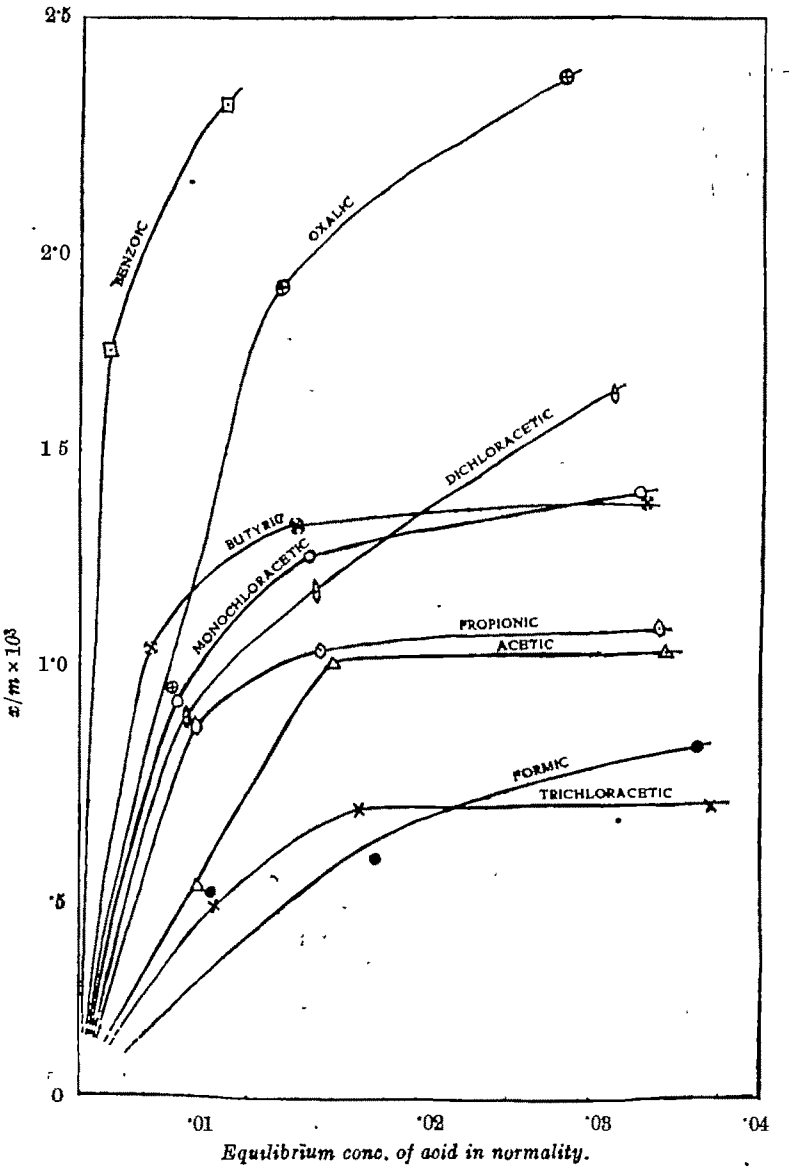
surface. The liberation of alkali from sodium chloride, as observed by Miller, is to be ascribed to the displacement of the free hydroxyl ions or anions of weak acids in the liquid side of the interface. The negative charge should be ascribed to the presence of an excess of anions on the surface (solid side of the interface). These anions may be chlorine or fluorine ions present in the preliminary purification or other anions formed on the surface of the charcoal. Traces of ammonia or amino bodies may also be present either from the atmosphere or formed during the process of activation from the nitrogen present. In one case an increase in the p_H of the conductivity water, used for washing a sample of activated sugar charcoal, has been observed (Table XV). The reversal of the charge from negative to positive on washing shows definitely that adsorption of ions (Mukherjee, *loc. cit.*) are primarily responsible for the charge of the charcoal surface and it is incapable of an explanation on the basis of Frumkin's theory. Though the negative charge cannot be explained from this theory, the positive charge is in agreement with Frumkin's theory, provided electrokinetic experiments can be assumed to indicate the charge in Frumkin's sense. On the other hand, a negatively charged oxygen charcoal (Kruyt and Kadt, *loc. cit.*) can adsorb alkali and it does not appear that there is any relationship between the electric charge and oxygen potential on the one hand and the charge and acid adsorption on the other in Frumkin's sense.

D. *Adsorption of Acids.*

Miller (*Technical Bulletin, Agricultural Experiment Station, Michigan State College*, 1925, **73**, 43) ascribed the liberation of alkali from salts by sugar charcoal to the capillary activity that is the capacity of the acid to lower the tension of the liquid-solid interface, so that an adsorption of the acid took place analogous to what takes place in a liquid-air interface. This point of view based on the classical theorem of Gibbs is wholly inadequate, as it does not distinguish between the adsorption of an ion or neutral molecule on the solid side of the interface from that on the liquid side (*vide*, Mukherjee, *Kolloid Z.*, 1929, **49**, 362). Besides considerations of capillary activity only lead us to expect liberation of alkali and not of acids. It will be seen later that both acid or alkali can be set free from a neutral salt or adsorbed from their solution (*cf.* Schilow), depending on the condition of preparing the charcoal which definitely goes against this theory.

FIG. 1.

Animal Charcoal (·25 g.).

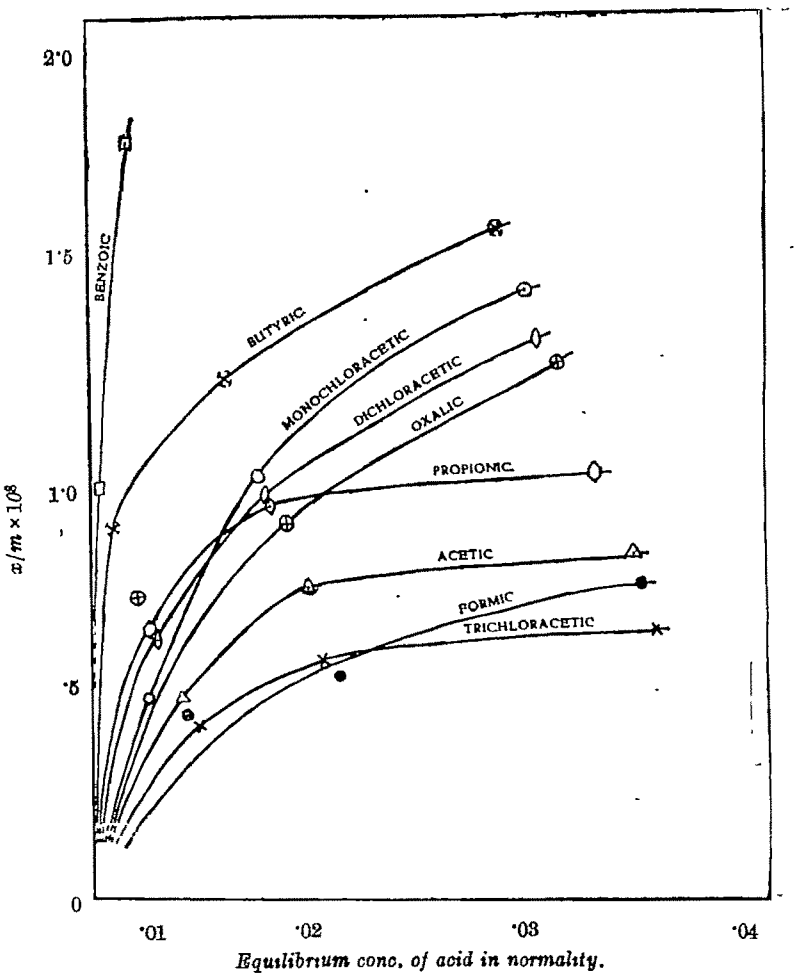


Equilibrium conc. of acid in normality.

Nekrassow (*Z. Phys. Chem.*, 1921, **136**, 22, 379; *cf.* also Dubinin, *loc. cit.*) finds that sugar charcoal exhibits a completely different adsorption of monobasic homologous organic acids in aqueous (also in alcoholic or ethereal) solution, from that shown by animal or blood charcoal. Traube's rule is valid for animal or blood

FIG. 2.

Animal Charcoal (·5 g.).

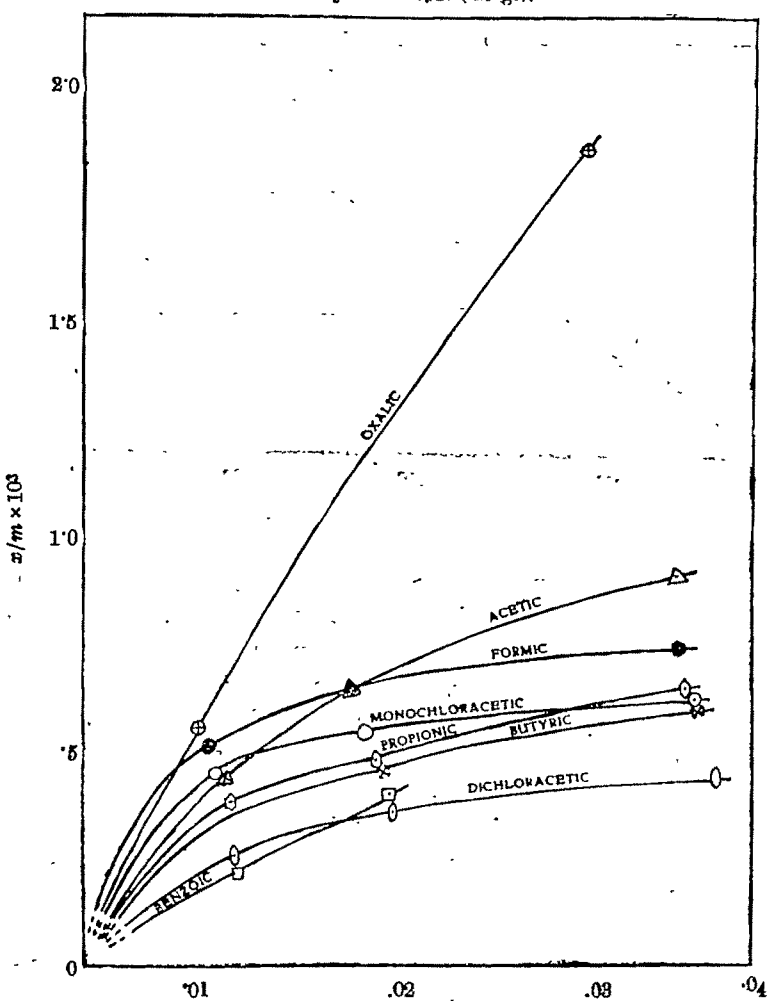


Equilibrium conc. of acid in normality.

charcoal but an inversely oriented series is observed for sugar charcoal. He attributed this to a difference in the crystalline structure of the charcoal. Dubinin (*loc. cit.*) obtained other orders of adsorption of such acids by charcoal, prepared from the same source, which were intermediate between these two inverse orders (" mixed series "), depending on the condition of activation. He considers that neither a difference in the structure nor the existence of the oxide B postulated by Schilow (*loc. cit.*) can explain the " mixed series." He ascribes the mixed series to variation in the effective adsorbing surface per unit mass. The latter depends on

FIG. 8.

Sugar Charcoal (·25 g.).



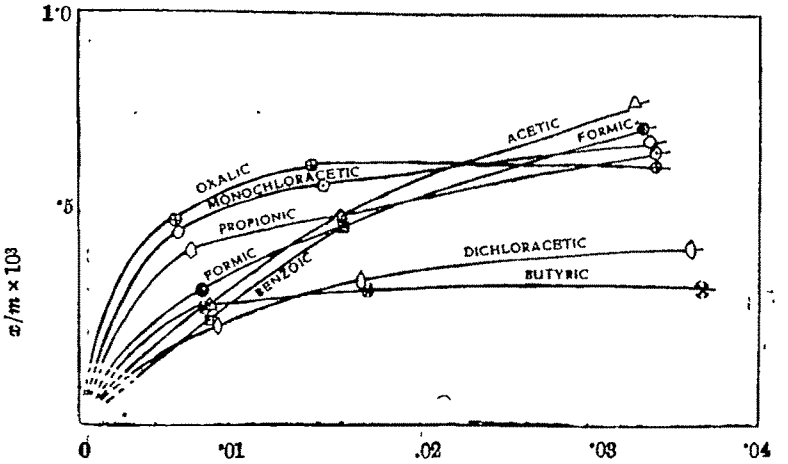
the size of the pores and of the molecules of the adsorbate. He also refers to the effect of the formation of the highly active oxide C (Schilow, *loc. cit.*) in inducing a reversal of the order of adsorption of organic acids. It is found however that the formation of the oxide C has not a uniform effect on the acid adsorption, *e.g.*, it does not affect the adsorption of heptylic acid.

EXPERIMENTAL.

Animal and sugar charcoals were prepared as described before. Jena glass bottles were employed and 50 c.c. of the solution were

FIG. 4.

Sugar Charcoal ('5 g.).



Equilibrium conc. of acid in normality.

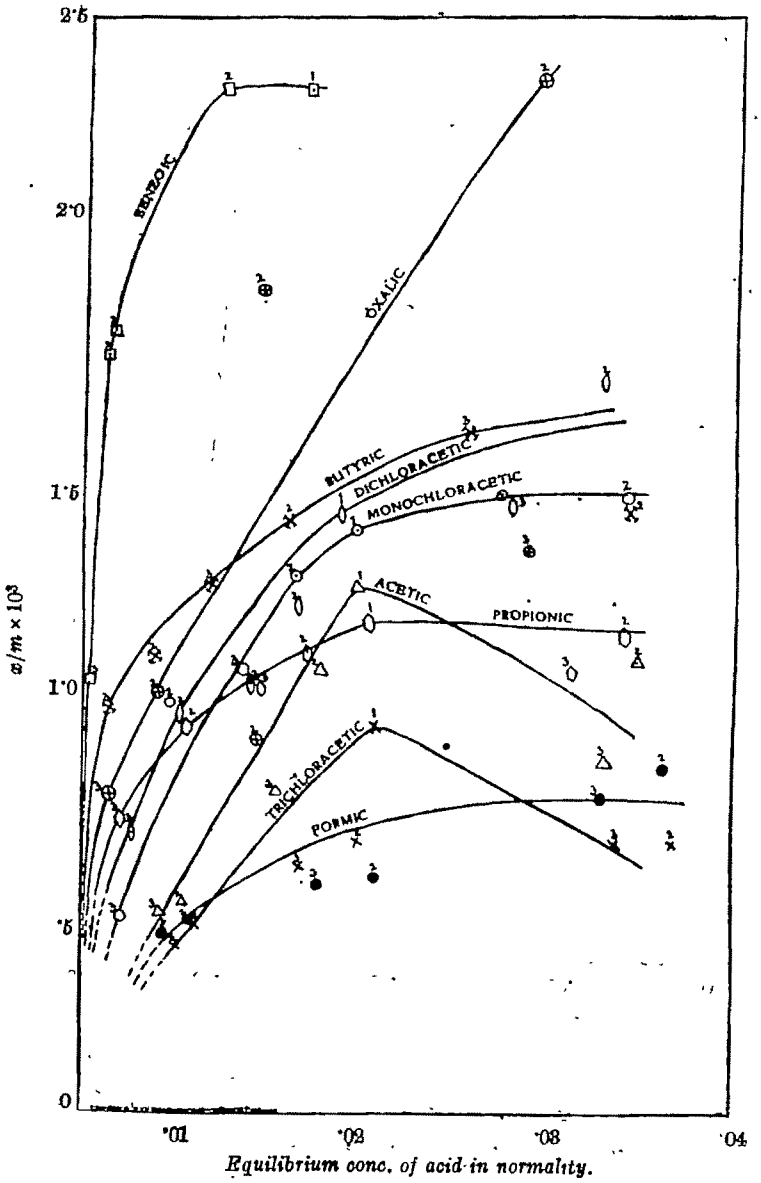
used in these experiments. The adsorbent was left in contact with the solution overnight after shaking for 2 hrs. 10 c. c. of the upper liquid were obtained by centrifugal action and titrated by baryta using phenol red as indicator. The concentrations are given in normality and the amount adsorbed in millimoles of the acid. The ash-content of animal charcoal was ·15 per cent. and zero for sugar charcoal. Three concentrations, ·01, ·02 and ·04 *N* were used. The results are given in the graphs (Fig. 1 to 4).

The continuous increase of the amount adsorbed with concentration and the tendency for the adsorbed amount to rise to a maximum (Fig. 1 to 4) disappears (Fig. 5 and 6) on plotting the results with different amounts of adsorbent in a single curve. This is very significant and shows that experiments with a constant mass of adsorbent (and constant volume of adsorbate) do not suffice as evidence of adsorption equilibrium between a *pure* adsorbent and a solute.

The order of adsorption of the acids brings out certain interesting features. In Table X the first, second and third columns give the decreasing order of adsorption of acids by animal charcoal ('5, ·25 and ·125 g. respectively), while the fourth, fifth and sixth columns give the orders with sugar charcoal, The seventh column shows the order of adsorption by blood charcoal (as given by Freundlich in Colloid and Capillary Chemistry, Eng. Ed., 1926. p. 198); the eighth by Fromageot (*Compt. rend.*, 1924, 179, 972); the ninth gives the

FIG. 5.

Animal Charcoal.



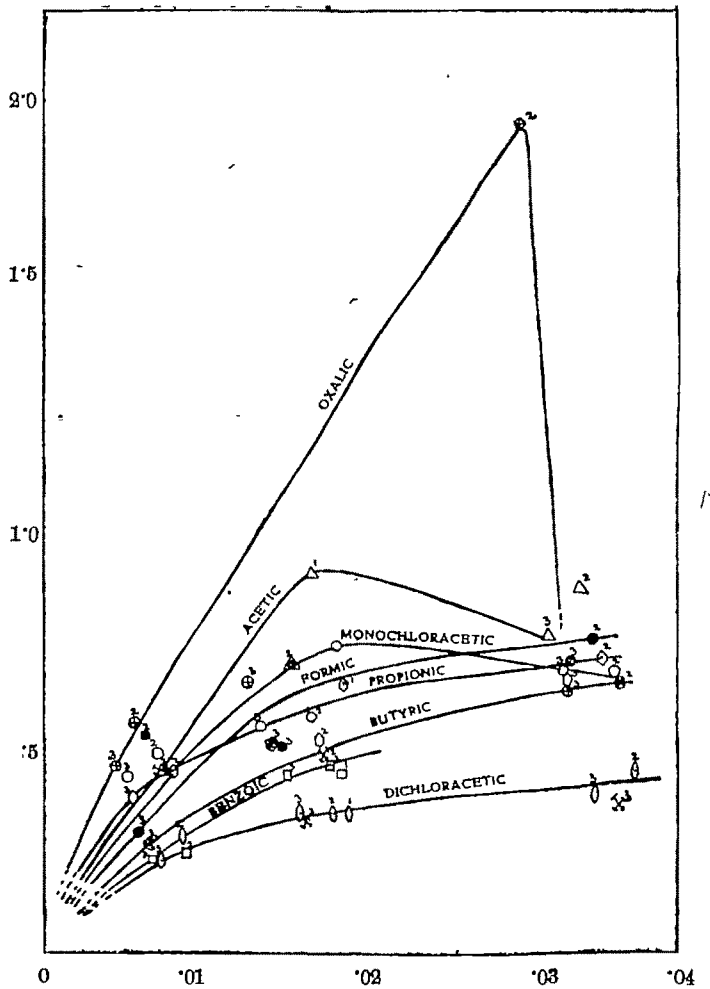
Equilibrium conc. of acid in normality.

Symbol 1 corresponds to ·125 g. of charcoal.
,, 2 ,, ·25 g. ,, ,,
,, 3 ,, ·5 g. ,, ,,

order of dissociation constants of the acids (Kohlrausch und Holborn, Das Leitvermögen Der Elektrolyte, 1916, p. 186) and the last that of

FIG. 6.

Sugar Charcoal



Equilibrium conc. of acid in normality.

Symbol 1 corresponds to ·125 g. of charcoal.
" 2 " ·25 g. " "
" 3 " ·5 g. " "

solubilities (Seidell, Solubilities of Inorganic and Organic Compounds, 1919). The numerals are explained below:—

(1) Benzoic, (2) oxalic, (3) butyric, (4) monochloracetic, (5) dichloracetic, (6) propionic, (7) acetic, (8) formic, and (9) trichloracetic.

TABLE X.

(1)*			(2)*			(3)*	(4)*			(5)*			(6)*	(7)**	(8)**	(9)**	(10)**
·01*N*	·02*N*	·04*N*	·01*N*	·02*N*	·04*N*	·02*N*	·01*N*	·02*N*	·04*N*	·01*N*	·02*N*	·04*N*	·02*N*				
1	1	1	1	1	1	1	2	2	7	2	2	2	7	1	2	$(3{\cdot}0 \times 10^{-1})$	7
3	3	3	3	2	2	5	4	4	2	8	8	7	4	3	6	$(3{\cdot}8 \times 10^{-2})$	9
2	4	4	2	3	5	4	6	6	4	4			6	4	8	$(5{\cdot}1 \times 10^{-5})$	4
6	5	5	4	4	4	7	8	7	6	3	4	6	1	5	7	$(1{\cdot}55 \times 10^{-3})$	2
5	6	2	5	5	3	6	7	8	8	7	6	4	5	9		$(2{\cdot}14 \times 10^{-4})$	1
4	2	6	6	6	6	9	3	1	1	6	3	3	9	6		$(6{\cdot}0 \times 10^{-5})$	
7	7	7	7	7	7		1	5	5	1	1	1				$(1{\cdot}8 \times 10^{-5})$	
8	9	8	8	8	8		5	3	3	5	5	5				$(1{\cdot}5 \times 10^{-5})$	
9	8	9	9	9	9		9	9	9	9	9	9				$(1{\cdot}3 \times 10^{-5})$	

* At 23°-25°. ** At 25°. † First dissociation constant.

The order depends on the mass of the adsorbent and is different for the two samples. Freundlich's order for blood charcoal* is the same (excepting trichloracetic acid) as that observed here with animal charcoal.* Fromageot's order of acid adsorption agrees approximately with the order obtained by us with sugar charcoal.

On examination of the individual results for the *animal charcoal*, oxalic acid shows the greatest irregularity and mono- and dichloracetic acids to a much smaller extent. Barring these acids the order of adsorption by animal charcoal is as follows:—

Benzoic > butyric > propionic > acetic > formic > trichloracetic. The curves for the pairs, formic & trichloracetic and mono- & dichloracetic, intersect each other. Assuming Freundlich's isotherm to hold good, it indicates that the two constants in the equation (α and β) are different for each of these pairs. The actual amount of its adsorption is almost the same with ·5 and ·25 g., though that calculated per unit mass when ·25 g. is used is double of that when ·5 g. is used. This observation makes it likely that equilibrium relations are not obtained with this acid. With sugar charcoal, oxalic acid again shows the greatest irregularity which is also the case though to a less extent with acetic, propionic and butyric acids. The two curves for different amounts of adsorbent have altogether dissimilar forms. It is difficult to speak of a definite order of adsorption independent of concentration.

Sugar and animal charcoals show a marked contrast. With the former, oxalic acid is most adsorbed, whereas benzoic acid takes the precedence in the case of the latter. Animal charcoal has on the whole, a greater adsorptive power than sugar charcoal. The irregularity with mono- and dichloracetic acids observed with animal charcoal is not observed with sugar charcoal, whereas the reverse occurs with acetic, propionic and butyric acids. The latter acids were Merck's extra pure and used without further purification. The irregularities with oxalic acid (animal charcoal) and acetic acid (sugar charcoal) are most marked. The adsorption of the four homologous aliphatic acids, formic, acetic, propionic and butyric by animal charcoal follows Traube's rule (Fig. 1 and

* Blood charcoal, as is known, contains a considerable percentage of iron and animal charcoal calcium, along with other impurities but the percentage of ash is different.

2). With sugar charcoal (Fig. 3 and 4) there is no definite order and Traube's rule fails for acetic, propionic and butyric acids (*cf.* Nekrassow, *loc. cit.*). The order of adsorption of the three chloracetic acids is the same in all cases, and agrees with their capillary activity (Freundlich, Colloid and Capillary Chemistry, p. 197).

It is difficult to say how far these differences result from the amount and nature of foreign substances or from differences in the size of the pores and of the adsorbed molecules or ions as suggested by Dubinin (*loc. cit.*). It is thus obvious from the work of Schilow, Dubinin and others and the present one, that the removal of acids from solution by activated charcoal does not admit of a simple explanation and is a very complicated process. The simplest possible explanation would be to ascribe the want of any regularity to the formation of different types of compounds (not merely oxides of carbon) during activation.

These observations also show that the order of adsorption of the different acids bear no relation to the order of solubilities (Bartell and Ying Fu, *J. Phys. Chem.*, 1929, **33**, 686).

E. *Equivalent Adsorption of both Ions of Acids.*

The equivalent adsorption of ions of hydrochloric and sulphuric acids observed by previous workers (Miller, *loc. cit.*, Kolthoff, *loc. cit.*) has been confirmed. Duplicate experiments were carried out. The total acidity was determined by titration and the chloride and sulphate estimated gravimetrically. 75 C.c. of solution were taken and concentrations are given in normality.

TABLE XI.

Hydrochloric Acid: Initial total acid conc. = ·0198N.

Amount (g.).	Final conc. total acid (N).	C_{Cl} total chlorine conc. (N).
1	·0174	·0177
,,	·0178	·0178
2	·0160	·0158
,,	·0160	·0162

TABLE XII.

Sulphuric Acid: Initial total acid conc. = ·0204*N*.

Amount (g.).	Final conc. total acid (*N*).	Total sulphate conc. (*N*).
1	·02	·0203
"	·02	
2	·0193	·0192
"	·0194	

It will be shown later from electro-osmotic experiments that excess adsorption of chlorine, hydrogen, hydroxyl and sulphate ions cannot be doubted. Obviously the assumption that equivalent adsorption of ions of an electrolyte, as obtained from analytical data, signifies *molecular* adsorption (that is, adsorption of neutral undissociated molecules of acids) is erroneous (*cf.* Fromageot, as also Phelps and Peters, *loc. cit.*). The total amounts of either ions present in the interface may be equivalent but the presence of one in excess on the solid side of the interface is responsible for the electro-kinetic potential drop in it.

F. *Effect of Ethyl Alcohol on the Adsorption of Acids by Different Samples of Charcoal.*

·5 G. of the charcoal and 100 c.c. benzoic acid (·01 *N*) containing different percentages of ethyl alcohol were shaken and kept overnight.

TABLE XIII.

Charcoal.	Ethyl alcohol.	Final conc. (*N*).	Amount of acid adsorbed (*g. mole*/*g* $\times 10^3$).
Blood charcoal (Merck's)	0	·0041	1·92
	1	·000456	1·91
	5	·000593	1·88
	10	·00091	1·82

Charcoal.	Ethyl alcohol.	Final conc. (N).	Amount of acid adsorbed ($g.\ mole/g. \times 10^3$).
Active carbon (Merck's)	0	·00273	1·45
	1	·00301	1·40
	5	·00356	1·29
	10	·00419	1·18
Sugar charcoal (activated and purified)	0	·00923	·15
	1	·00968	·064
	5	·00968	·064
	10	·00968	·064
Animal charcoal (activated and purified)	0	·00225	1·55
	1	·00248	1·50
	5	·00315	1·37
	10	·00388	1·23

Michaelis considers that (Freundlich, Colloid and Capillary Chemistry, *loc. cit.*) non-electrolytes can displace neutral molecules of electrolytes but not the ions individually. Kolthoff (*loc. cit.*) also holds that capillary-active non-electrolytes can displace strong acids. In the present case, the formation of esters is not likely and the decrease in adsorption with the concentration of alcohol observed with *active carbon* and animal charcoal indicates the displacement of the adsorption of the acid. This observation is consistent with the higher capillary activity of alcohol, assuming that the surface tension changes in an air-liquid interface are parallel to those of a solid-liquid interface, where the liquid is the same. The results however do not show a uniform effect of the concentration of the alcohol and depend on the sample used. It is necessary to point out also that such consideration of capillary activity on the basis of Gibb's theory of adsorption and deduced from analytical measurements overlooks the distribution of the ions between the solid and the liquid side of the interface and is of no value in deciding whether the adsorption is *molecular* (*i.e.*, of undissociated molecules) or ionic.

G. *Hydrolytic Adsorption and Electrical Charge of the Charcoal Surface.*

The charcoal was prepared, purified, activated and preserved, as previously described (600°, 6 hrs.). The charcoal and the solution were kept in Jena glass bottles overnight after the mixture has been well shaken. The upper liquid obtained with the help of a centrifuge was titrated. Its p^H was also measured by an indicator set. The concentrations of electrolytes in the following tables are given in normality:

Electro-osmotic Experiments: Carried out as described in section C.

TABLE XIV.

·5 G. of charcoal was treated with 50 c.c. of electrolyte.

Sample I. Animal charcoal: negatively charged (ash·15%).

Electrolyte.	Initial conc. (*N*).	Final conc. (*N*).
HCl	·01	·01
KOH	·01	·007
KCl	·01	·0086(acid)

Sample II. Purified Animal charcoal*: positively charged (ash·15%).

HCl	·0097	·00824
KOH	·0097	·00756
KCl	·0097	(Neutral)
KCl	·00485	(Neutral)

* This sample contained 74·2% water. In weighing the charcoal and in calculating the initial concentration of electrolyte added, the necessary correction was made.

TABLE XV.

Sugar charcoal: positively charged (ash-0 %)—Sample A.

Volume of Electrolyte = 50 c.c.

Electrolyte.	Amount of charcoal (*g.*).	Final conc. (*N.*)	Titre (c.c.) of ·02 *N*-HCl or —KOH for 10 c.c. of soln. after adsorption.	Final Conc. (*N*) & pH.
Water (pH, 6·8)	·125	—		7·2 pH
	·25	—		7·2
KCl (pH, 6·7)	·125	·02	—	7·9
	·25	·02	—	7·9
KCl (pH, 6·7)	·125	·01	—	7·9
	·25	·01	—	7·9
HCl	·125	·02	9·5	·0196 *N*
	·25	·02	9·45	·0189
HCl	·125	·01	4·8	·0096
	·25	·01	4·65	·0093
CH_3COOH	·125	·02	9·15	·0183
	·25	·02	8·35	·0167
CH_3COOK (pH, 7·0)	·125	·02	—	7·9 pH
	·25	·02	—	7·9
CH_3COOK (pH, 7·1)	·125	·01	—	7·7
	·25	·01	—	7·7
KOH	·125	·02	10	·02 *N*
	·25	·02	10	·02

TABLE XVI.

Effect of the Addition of Neutral Electrolytes on the Adsorption of Hydrochloric Acid.

Sugar charcoal: positively charged—Sample B.

·5 *G.* charcoal + 100 c.c. solution.

Solution.	Initial acidity.	Acidity after contact with charcoal.	Amount absorbed (*g. mole./g.* × 10^3).
Water	(pH) 6·7	(pH) 6·7	—
·01 *N*-KCl	,, 6·7	,, 6·9	—
·01 *N*-$BaCl_2$	,, 6·8	,, 6·8	—
·01 *N*-HCl	·01 *N*	·00952 *N*	·096
·01 *N*-HCl + ·01 *N*-KCl	·01 *N*	·00952 *N*	·096
·01 *N*-HCl + ·01 *N*-$BaCl_2$	·01 *N*	·00952 *N*	·096

Effect of Electrolytes on the Charge of Different Samples of Charcoal.

The following samples were obtained by activation after purification as usual.

TABLE XVII.

(Sugar charcoal: ash-negligible).

	Movement of bubble.			
	HCl		H_2SO_4	NaOH*
Concentrations.	Sample 1	Sample 2	Sample 3	Sample 1
0	+1·5	+1·3	+·13	+·9
·0001*N*	−·25	−·35	−·1	−·25
·0002*N*	−·25	−·4	−·45	−·38
·001*N*	+1·0	+·78	−3·0	−·91

TABLE XVIII.

Movement of bubble.

	Animal charcoal : ash-·15 per cent.			Blood charcoal : ash-·31 per cent.	
	HCl	NaOH		HCl	H_2SO_4
Concentrations.	Sample 1	Sample 1	Sample 2		
0	+1·08	+·81	+·76	+2·1	+2·1
·0001*N*	+2·35	+2·15	+1·85	—	—
·0002*N*	+4·75	+1·7	+2·23	+4·0	+2·54
·001*N*	+1·4	+1·16	—	+1·5	+1·91
·008*N*	—	−·99	−4·8	—	—

TABLE XIX.

Movement of bubble.

	Merck's activated carbon : ash-7·5 per cent.	Gelatin charcoal : ash-6·2 per cent.
Concentrations.	HCl	H_2SO_4
0	+·8	+·2
·0001*N*	+1·16	—
·0002 *N*	+3·1	−·45
·001 *N*	—	−1·15
·008 *N*	+5·2	—

* The adsorption of atmospheric carbon dioxide should be taken into consideration in interpreting the results.

The negatively charged animal charcoal does not adsorb acid but adsorbs alkali. In contact with potassium chloride, it liberates acid. The above sample, if further purified by washing, adsorbs (more acid and less alkali; also no free acid or alkali (as measured by titration) is liberated from potassium chloride. Sugar charcoal adsorbs acid but not alkali; it liberates alkali from neutral potassium chloride. The absorption of acid from potassium chloride and the p_H of the wash-water depend on the sample (A, B).

Sample 'A' definitely contains traces of an alkaline substance. In section B, it has been pointed out that this charcoal contains impurities possibly of an alkaline nature. The adsorption of acid is also smaller with "B.' Neutral chlorides have no effect on the adsorption of hydrochloric acid. From an examination of the data (Section A), it will be evident that the irregular effect of the mass of the adsorbent is absent with animal charcoal, when activated after the usual purification with carbon dioxide (Section A, Tables I and II). When however nitrogen is used (Table III), a greater adsorption than that indicated by the equilibrium concentration of the acid is observed, when the mass of the adsorbent is increased. This observation is also in agreement with the assumed presence of alkaline substances. Animal charcoal differs from sugar charcoal in this regard. The initial negative charge as also the fact that after washing the acid adsorption increases, the alkali adsorption decreases and the charge becomes positive, point to the presence of acidic impurities in the negatively charged animal charcoal. The primary adsorption of anions is further supported by the observation that Merck's animal charcoal (from which our samples of animal charcoal have been prepared), is positively charged (Table IX), but after treatment with acids and preliminary washing, it acquires a negative charge and becomes positive only on further careful purification, (Section I). Moreover, positive animal charcoal adsorbs benzoic acid more than the negative does.

TABLE XX.

100 C.c. of benzoic acid taken: time of contact = 20 hrs.

Amount of charcoal taken = 25 g.

Sample.	Initial conc. (*N*).	Final conc. (*N*).	Amount adsorbed (*g. mole*/*g.* $\times 10^3$).
Negatively charged animal charcoal	·021	·0178	1·98
Positively charged animal charcoal	·0107	·015	2·38

It is thus clear that contrary to Schilow's postulates, the excess adsorption (primary) of both cations and anions of the solid side of the interface has to be taken into account.

Sugar charcoal.—Positively charged sugar charcoal (Table XVII) becomes negatively charged in presence of very low concentrations of hydrochloric acid. It becomes again positive at higher concentrations. With sulphuric acid and sodium hydroxide, the charge remains negative within the same range of concentration. That the solid side of the interface can react with hydrogen, hydroxyl, sulphate and chlorine ions is established by these results and distribution of ions in Mukherjee's sense (*loc. cit.*) has to be taken into account. The conception of the formation of an ionogen complex (Pauli and Valko, *Z. Phys. Chem.*, 1926, 121, 161, also Pennycuick, *J. Chem. Soc.*, 1930, p. 1447) suffers from an obvious defect though commonly overlooked. The formation of an ionogen complex does not explain why one part of it (a component ion of the complex) will remain fixed on the solid surface and the other in the mobile sheet of the double layer. The initial poositive charge followed by a negative and then a positive charge (sugar charcoal and hydrochloric acid) show clearly that attention should be focussed on the fixation. Also the conclusion of Phelps and Peters (*loc. cit.*) and of Fromageot (*loc. cit.*) that charcoal selectively adsorbs non-dissociated molecules of acids and not ions are not borne out by the above.

Ogawa (*loc. cit.*) found that sugar charcoal treated with acid becomes positively charged and when treated with alkali is negatively charged. Our results confirm this. Also Miller's observation (*loc. cit.*) that sodium hydroxide is not adsorbed by purified sugar charcoal is confirmed. Miller and Kolthoff (*loc. cit.*) have sometimes observed negative adsorbtion of the alkali.

The enhancing effect of sodium hydroxide on the negative charge (Table XVII) indicates two possibilities: (*i*) the adsorbed cations present in the solid side of the interface are partially displaced by ions in the mobile layer so as to increase the free negative charge, (*ii*) the increase is due to the primary adsorbtion of hydroxyl ions either as such or as forming anions with electrolytes present in the surface. The absence of adsorption of sodium hydroxide together with the negative adsorption of alkali recorded in some instances (*loc. cit.*) may be best reconciled as indicating presence of *basic* salts. With higher temperature of activation, there is a marked fall in the amount of adsorption (Section A; see also Frumkin and

Schilow, *loc. cit.*). It may indicate loss of the electrolytes present on the surface.

The high adsorptive capacity of sample J (Section B), which was heated for 4 hrs. at 900°, indicates however that the presence of impurities of a basic nature is not the only factor determining the adsorption. In this instance the adsorption does not depend on the mass as in the other cases and increases regularly with the equilibrium concentration of the acid and at the same time the adsorption is quite marked. The nature of the charcoal surface is a factor which has to be taken into account. We also conclude that activated sugar charcoal prepared after Miller (*loc. cit.*) possibly contains removable impurities.

Animal, Blood and Gelatin Charcoal and Merck's Active Carbon (purified and activated as usual).—These charcoals contain an appreciable percentage of ash. It is not surprising that they behave differently in contact with electrolytes. They all become positively charged with hydrochloric acid and do not show the negative charge at low concentrations of the acid observed with sugar charcoal. Both animal and blood charcoals (ash-content—·15% and ·81% respectively) show a diminution of the positive charge at ·301*N*. With the charcoal obtained from Merck's active carbon, which has a higher ash-content (7·5%), the positive charge increases even at ·008*N*. The amount and the nature of the inorganic substances probably play a very important part. The samples behave as complex systems and have different properties.

With sulphuric acid (Tables XVII, XVIII and XIX), sugar and gelatin charcoals show a similarity in the results but a contrast to blood charcoal, though the gelatin charcoal contains 6·2% ash and sugar charcoal is practically free from it. This again shows that the ash-content is not the only factor. The manner of activation has a definite influence. It is probably the determining factor, so far as the organic impurities and the structure of the surface are concerned. The nature of the inorganic as also perhaps of the organic impurities and the structure of the solid side of the interface should also be considered.

With sodium hydroxide, animal charcoal (Table XVIII) shows an *increase in the positive* charge and becomes negative only at ·008*N*. The initial increase in the positive charge is consistent with the assumption of the presence of cations and anions on the surface. It

indicates that the anions combine with the alkali and pass out of the interface. At higher concentration, the adsorption of hydroxyl ions or of the anions formed in the above manner diminishes the positive charge and makes it ultimately negative. Umetsu (*loc. cit.*) made the following observations: (*a*) blood charcoal has a negative charge in moderate dilution of sodium hydroxide (·01*N*); it is negatively charged in rather dilute hydrochloric acid solution (up to ·00145*N*) and in the more concentrated acid solution the charge becomes positive. With sulphuric acid, it has a negative charge up to ·00143*N* and a positive at higher concentrations. (*b*) Sugar charcoal was however found to have a negative charge throughout the same range of concentrations of hydrochioric acid. He used Merck's blood charcoal, which we find to be negatively charged and which becomes positive on purification.

Ogawa (*loc. cit.*) working with *normal* and activated sugar charcoal (ash-free) records that the latter has no charge (iso-electric) in ·002*N* sodium hydroxide solution and negative in ·02*N*. In neutral (·02*N*-KCl solution) and hydrochloric acid solutions (·02*N* and ·002*N*), the charge was found to be positive. There are no data at other concentrations or in contact with pure water. His observations are in agreement with our resuls (Table XVII), in so far as the behaviour at higher concentrations of HCl and NaOH are concerned. In dilute acid and alkali concentrations (·001*N* and ·0002*N*), it is negatively charged and in these respects the results are different from those observed by Ogawa.

Neither Umetsu nor Ogawa observed however the two-fold reversal in the sign of the charge of sugar charcoal from positive to negasive at low concentrations and from negative to positive at high concentrations with hydrochloric acid (Table XVII). The above differences show again that inorganic substances are not alone responsible for the different properties of charcoal as both samples are free from ash-

The preceding observations establish clearly that the nature of the electrolytic impurities, of the electric charge and the hydrolytic adsorption are correlated and in fact, in a manner which is in accord with the postulates of Mukherjee. As stated before, considerations of interfacial tension overlook the manner of distribution of ions in the interface. Apart from this, it cannot account for (*a*) the variations of charge on washing, (*b*) the relation between the charge and

the adsorbabilities of acid and alkali and (*c*) the role of the charge in determining whether hydrolytic adsorption results in liberation of acid or alkali and (*d*) the dependence of the charge on impurities.

The adsorption of acid and alkali and hydrolytic adsorption in relation to the theories referred to in the introduction will be further dealt with in the second part.

Summary.

I. Reference has been made in the introduction to the important role, which the electric charge of adsorbent plays in adsorption processes. The theories of Frumkin and Schilow have been criticised in the light of recent experimental data of Dubinin, Kruyt and also of the author and of Mukherjee and co-workers.

2. An anomalous effect of mass of charcoal, obtained from different sources and activated under different conditions, on the absorption of benzoic acid has been examined. The presence of substances other than carbon on the surface of the charcoal is indicated. The amount and nature of these foreign substances depend on the conditions of activation. Sometimes a lower end-concentration of solute has been found to produce greater adsorption per unit mass, when the total mass of the adsorbent increases and sugar charcoal has been found to show the greatest discrepancy in this respect. The result cannot be explained by an adsorption equilibrium or by neutralisation process and indicate that complicated processes are at work.

3. All samples of charcoal after careful purification and washing have been found to acquire a positive charge in contact with water. From Mukherjee's point of view, pure charcoal in contact with water should acquire a positive charge due to preferential primary adsorption of hydrogen ions as compared to hydroxyl ions or basic cations present in the charcoal. The initial negative charge observed with some samples should be ascribed to the presence of an excess of anions on the surface (solid side of the interface). Traces of ammonia or amino bodies may be present either from the atmosphere or formed during the process of activation from the nitrogen present.

4. The order of adsorption of organic acids by charcoal has been found to be different for different samples. The adsorption curves intersect each other in some cases. The curves for different amounts of the same sample have altogether dissimilar forms. The order cannot be explained by *capillary activity* or from chemical considerations such as the dissociation constant or the solubility. The orders of adsorption resemble the *mixed series* observed by Dubinin, with this difference that the order depends also on the amount of the adsorbent. This latter observation cannot be accounted for by considerations of available pore-space advanced by Dubinin for the *mixed series*. It cannot also be due to the formations of the oxides A, B or C as postulated by Schilow, as the observations show that there is scarcely any regularity as to the formation of different types of compounds on the surface of the charcoal.

5. The equivalent adsorption of the anion and the cation of hydrochloric and sulphuric acids found by previous workers has been confirmed. It has been pointed out that the assumption that equivalent adsorption of ions of an elcctrolyte as obtained from analytical data signifies *molecular* adsorption is erroneous.

6. Ethyl alcohol decreases the adsorption of benzoic acid but the results depend on the sample used.

7. Negatively charged animal charcoal adsorbs only alkali and not acid, positively charged animal charcoal adsorbs both acid and alkali.

8. Activated sugar charcoal adsobs only acid and not alkali. Neutral solution in contact with sugar charcoal becomes alkaline. This confirms the observation of Bartell and Miller.

9. Measurements of charge of sugar charcoal in contact with acid and alkali solutions indicate that the condition in the solid side of the interface has to be distinguished from that in the liquid side. The adsorption of ions of one sign in excess on the solid side is clearly demonstrated. OH', $H^{\cdot}$, Cl' and SO_4'' ions can be adsorbed on the solid side.

It gives me great pleasure to express my thanks to Prof. J. N. Mukherjee for suggesting this work and for facilities. I am also thankful to the authorities of the University of Calcutta

for awarding me a research scholarship, which has enabled me to undertake this work.

PHYSICAL CHEMISTRY LABORATORY,
THE UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA.

Received January, 1, 1931.

Addenda (*August*, 8, 1931.)

The following papers having a bearing on the present communication have since been published. It is proposed to deal with these in a subsequent communication. Bruns, *Kolloid Z.*, 1931, **54**, 33; *Z. Phys. Chem.*, 1931, **155**, 77; Frumkin, *Z. Phys. Chem.*, 1931, **155**, 41; Kruyt, *Koll.-Chem. Beih.*, 1931, **32**, 249.

A Note on the Main Constituents of the dried Rind of the Fruit of *Garcinia Gambogia*.

By K. I. Kuriyan and Kantilal C. Pandya.

Sudborough and Vridhachalam have investigated the tartaric acid content of tamarind (*J. Indian Inst. Sci.*, 1920, 3, 61) and Bathum and Nigam have also investigated tamarind as a source of alcohol and tartaric acid (*Bull. Agr. Res. Inst. Pusa*, 1924, No. 153). No work appears to have been done on *Garcinia Gambogia*, the dried rind of the fruit of which finds a wide use in Cochin, Travancore and South Malabar, as a condiment, very much as tamarind and kokum (*G. Indica*) are used in other parts of the country. "Kadumpuli," as the dried rind of the fruit of *G. Gambogia* is known in Malayalum, is now found to contain about 10% of tartaric acid.

Experimental.

The rind (10 g.) was refluxed with 200 c.c. of water. The filtered extract, on neutralisation with ammonia gave a flocculent precipitate containing iron, calcium, magnesium, phosphate and tartrate. The filtrate showed the presence of sodium, potassium, citrate, tartrate, and reducing sugar. The inorganic constituents were confirmed by the analysis of the ash obtained by incinerating the dried rind.

Free Acids.—The rind (10 g.) was four times extracted with definite quantities of boiling water, till free from acids. The accumulated extracts, made up to a known volume, were titrated against standard sodium hydroxide solution, using phenolphthalein as indicator. 100 G. of the rind required 11·48 and 11·45 g. of sodium hydroxide respectively in two determinations.

Extracts.

Name of the constituents found.	Aqueous.	Acid.	Alkaline.	Method of determination
(*a*) Tartaric acid as potassium hydrogen tartrate.	10 p. c.	(1) 12·5 p. c. ... (2) 9·3 p. c.		Goldenberg's method (Sudborough and Vridhachalam, *loc. cit.* p 65, 50 g. of material employed each time.
(*b*) As Ba-salt = potassium hydrogen tartrate = tartaric acid	4·11 g. 13·6 p. c. 10·6 p. c.	4·09 g. 13·6 p. c. 10·6 p. c.	4·16 g. 13·7 p. c. 10·7 p. c.	8 G. of material employed each time. The Ba-salt was prepared by a method which was analogous to to that of Sudborough and Vridhachalam for Ca-salt (*loc. cit.*, p. 66).
Phosphoric acid as calcium triphosphate	1·52 p. c.	1·52 p. c.	1·54 p. c.	Determined by means of uranium nitrate.
Reducing sugars as glucose.	7·4 p. c.	(1) 15·1 p. c. (2) 15·2 p. c.	14·8 p.c.	By means of standard Fehling's solution. The two acid extracts contained 10 and 15 c.c. of conc. HCl respectively.

N.B.—Polarimetric determinations were not helpful as concentrated extracts were not clear, and clear solutions were too dilute.

CHEMISTRY DEPARTMENT,
ST. JOHN'S COLLEGE, AGRA.

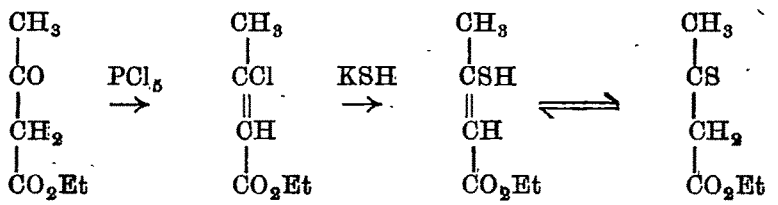
Received April 8, 1931.

Thioketonic Esters. Part I. Synthesis of Ethyl Thioacetoacetate and its Derivatives.

By Susil Kumar Mitra.

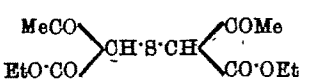
The present investigation was taken up with a view to observe more rigidly the existing similarity between C:S and C:O groups. It was also thought necessary to observe whether the CS-group can impart any negative character to the adjacent CH_2-group like the carbonyl group in diketones and ketonic esters.

The present paper describes the preparation and properties of ethyl thioacetoacetate* $Me{\cdot}CS{\cdot}CH_2{\cdot}CO_2Et$ which has been synthesised thus:.



The mercaptan which is thus formed in the course of the reaction, evidently tautomerises to the keto-form which is supported by subsequent estimation of keto-enol by Meyer's method of bromination. The substance was subjected to ketonic hydrolysis with a view to obtain thioacetone $(Me)_2CS$. The compound does not react with sodium carbonate or bicarbonate. On boiling with dilute sulphuric acid it

* A compound named as "ethyl thioacetoacetate" was first prepared by Buchka (*Ber.*, 1885, 18, 2090) and later on by Michaelis, Phillips and Delisle (*Ber.*, 1890, 23, 559; 1887, 20, 2038) and Schonbrodt (*Annalen.*, 1889, 253 168) by the action of sulphur dichloride on monosodioderivative of ethyl acetoacetate. But a wrong nomenclature has really been applied to the compound, as it is a true sulphide and the constitutional formula is

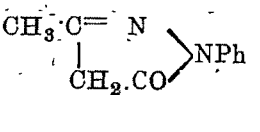


which afterwards was confirmed by Buchka and Sprague (*Ber.*, 1889, 22, 2541).

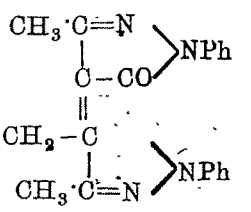
evolves carbon dioxide profusely like ethyl acetoacetate along with some sulphuretted hydrogen proving that it contains an esterified carboxyl group. On completion of hydrolysis no oil was found to be left behind. Evidently if ethyl thioacetoacetate had got the constitution $CH_3 \cdot CS \cdot CH_2 \cdot CO_2Et$ then on subjecting it to ketone hydrolysis it should have yielded thioacetone along with carbon dioxide. But if thioacetone had actually been formed, it evidently suffered decomposition in the course of the reaction, which is in accordance with Baumann and Fromm (*Ber.*, 1889, **22**, 2592) who during the preparation of trithioacetone suspected the formation of thioacetone as a readily decomposing volatile oil. In the end of the process the presence of acetone in the solution was ascertained. It, therefore, follows that thioacetone actually resulted in the course of hydrolysis according to the equation, $CH_3 \cdot CS \cdot CH_2 \cdot CO_2Et = CH_3 \cdot CS \cdot CH_3 + CO_2 + EtOH$, and the thioacetone was decomposed by water into acetone and sulphuretted hydrogen. Similar results were obtained when it was boiled with dilute caustic potash.

It was also noticed that the same ester always results by the action of potassium hydrosulphide on the *cis*- or *trans*-chlorocrotonic ester, and hence it was unnecessary to separate the isomers. The ethyl thioacetoacetate thus prepared was found to behave as a true ketone. With phenylhydrazine, hydroxylamine and aniline it evolves copiously sulphuretted hydrogen even in the cold. On treating the ester with phenylhydrazine in the cold and completing the reaction on a water-bath, Knorr's phenylmethylpyrazolone (I) was obtained quantitatively along with a quantity of its dehydro-product (II).

$$CH_3 \cdot CS \cdot CH_2 \cdot CO_2Et + NH_2 \cdot NH \cdot Ph \rightarrow$$



(I)



(II)

The reaction on being performed with a little excess of phenylhydrazine, nearly 50% of the ester was converted into the dehydro-product (II). The ester on being treated with *p*-nitrophenylhydrazine,

and phenylhydrazine-*p*-sulphonic acid yielded the corresponding pyrazolones.

The ester was found to react with metallic sodium with brisk evolution of hydrogen in ethereal suspension like ethyl acetoacetate and the sodium derivative was thrown down as a white powder. This is so very hygroscopic that it was found to be extremely difficult to analyse. Further investigations of the compound and analogous compounds are in progress.

EXPERIMENTAL.

Ethyl Thioacetoacetate.—Ethyl chlorocrotonate (100 g.) was treated with potassium hydrosulphide (48 g.) at 0°. The reaction ensued instantaneously and potassium chloride began to separate. The reaction was then completed on a water-bath under reflux for two hours. The whole of the mixture was then diluted with water when the major portion of the oil settled at the bottom and then after acidifying the supernatant liquid, the oil was extracted by means of ether. The ethereal extract after drying over anhydrous sodium sulphate was freed from ether and subjected to vacuum distillation. The fraction coming between 60° and 110° at 15 mm. was refractionated and the portion boiling at 75°/15 mm. was found to be pure ethyl thioacetoacetate (yield 30%): $d_{31}^{\circ}=1{\cdot}0554$ and $n_{26}^{\circ}=1{\cdot}4712$. (Found: C, 50·06; H, 7·02; S, 21·3; M.W., 144. $C_6H_{10}O_2S$ requires C, 48·3; H, 6·9; S, 21·9 per cent.; M.W., 147).

Ethyl thioacetoacetate is an orange, mobile liquid possessing sweet ester-like smell. It can decolourise an alcoholic solution of iodine proving the existence of the SH-group. It evolves sulphuretted hydrogen in contact with phenylhydrazine, hydroxylamine, toluidine, etc. in the cold. On boiling with 10% sulphuric acid it is completely transformed into acetone, sulphuretted hydrogen and carbon dioxide in 4 hours. Similarly with 10% caustic potash or soda, alkali sulphides and acetone are produced. On boiling with the theoretical amount of alcoholic caustic potash, a white precipitate is obtained. The amount of potassium in the compound indicated that it was a mixture of potassium salts of thioacetoacetic and acetoacetic acids. Evidently it points out that in the course of hydrolysis the ketonic sulphur had partially been replaced by oxygen, and the presence of potassium sulphide was proved in the

alcoholic extract. In the presence of metallic sodium in ethereal suspension it vigorously evolved hydrogen and formed the sodium derivative as a white powder. The sodium derivative was found to be very hygroscopic. The ester on being added to an alcoholic solution of sodium ethoxide in molecular proportions gave no precipitate, which evidently led to the conclusion that the monosodio-derivative is soluble in alcohol.

Phenylmethylpyrazolone.—Ethyl thioacetoacetate (5 g.) was treated with phenylhydrazine (3·5 g.) in the cold, and allowed to remain for 4-5 minutes when the vigorous evolution of sulphuretted hydrogen ceased. The reacton was completed by heating on a water-bath for 4 hours. It was then washed with ether to remove the resinous matter and then digested with warm alcolol, when the pyrazolone (m.p. 127°) dissolved leaving behind the less soluble dehydro-product (yield 60% of pyrazolone and 20% of the dehydro-product). (Found: N, 16·28. $C_{10}H_{10}ON_2$ requires N, 16·09 per cent.).

Dehydrophenylmethylpyrazolone.—The ester (5 g.) was heated with double the amount of phenylhydrazine on a water-bath for 6 hours. The resulting product was washed with ether, and then with alcohol. The residue was crystallised from acetic acid. It began to char at 246° and finally decomposed completely at 320° (yield 50%). (Found: N, 16·97. $C_{20}H_{18}ON_4$ requires N, 16·96 per cent.).

Phenylmethylpyrazolone-p-sulphonic Acid.—The ester (3 g.) and phenylhydrazine-*p*-sulphonic acid (4 g.) were heated on a water-bath for 6 hours. The reaction mixture was then digested with hot water and the first and the second crop of crystals that separated were collected and found to melt with decomposition at 320° (yield 70%). (Found: N, 11·02. $C_{10}H_{10}N_2O_4S$ requires N, 11·02 per cent.).

p-*Nitrophenylmethylpyrazolone* was similarly obtained. The reaction product was washed with petroleum ether and finally crystallised from alcohol, m.p. 218° (yield 40%). (Found: N, 19·32. $C_{10}H_9O_3N_3$ requires N, 19·18 per cent.).

My best thanks are due to Sir P. C. Rây for the kindest interest he has taken in this investigation.

PALIT PROFESSOR'S LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
CALCUTTA.

Received June 23, 1931.

Mercuration of Higher Aromatic Hydrocarbons. Part I.

By M. Goswami and H. N. Das-Gupta.

Various organo-mercuric compounds having mercury attached directly to the carbon atom of aliphatic or aromatic radicles have been prepared. In recent years attention has been directed more to the preparation of mercuri-aromatic compounds containing as low a percentage of mercury as possible, as, for therapeutic purposes, barring toxicity, they have been found in their bactericidal activity far superior to organo-arsenic compounds—the toxicity being due to the high percentage of mercury which must be diminished to the lowest possible limit before it could be used successfully in therapeutics. With this end in view the compounds described in this paper were prepared by the method of Dimroth (*Ber.*, 1898, **31**, 2154; 1899, **32**, 758). It appears from literature, that except in the cases of benzene, naphthalene and diphenyl, no attempt has been made to prepare mercury derivatives of higher aromatic hydrocarbons.

Anthracene, phenanthrene, acenaphthene and fluorene all gave the corresponding monomercurichloride compounds and of these the last two gave the corresponding mercurihydroxides whilst the mercurichlorides of anthracene and phenanthrene failed to produce similar hydroxides by the ordinary method. These mercurihydroxides behave generally like the ordinary aromatic mercurihydroxides evolving ammonia from ammonium chloride. The position which is taken up by the mercury atom has not yet been settled and we propose to undertake this problem in the near future. Determinations of toxicity and therapeutic index of the compounds are in progress.

Experimental.

Acenaphthene Mercurichloride.—Acenaphthene (10 g.) and mercuric acetate (24 g.) were dissolved in acetic acid (70 c.c.) and

the solution was heated under pressure in an oil-bath to 115-20° for 5 hours. During this period the colour of the solution turned red. This was then allowed to cool whereby some unacted acenaphthene together with mercurous acetate separated out. The filtrate from the unchanged mass, etc., was now evaporated to one third the original volume and was treated with alcoholic calcium chloride solution after cooling. This resulted in the precipitation of a slightly pink-coloured compound which was filtered and the residue was repeatedly washed with water and alcohol and finally with ether. The mass was then dried in a vacuum desiccator; the dried mass thus obtained was pinkish-white in colour. It melts with decomposition at 148° (yield 80 per cent.). It is insoluble in most of the common organic solvents. (Found: Hg, 50·59, 51·05; Cl, 9·06. $C_{12}H_9HgCl$ requires Hg, 51·32; Cl, 9·12 per cent.).

Anthracene Mercurichloride.—Mercuric acetate (10 g.) and anthracene (5 g.) were first of all dissolved in acetic acid (45 c.c.) and the solution was heated under pressure to 130-40° and kept at that temperature for 7-8 hours. In course of one hour the whole of anthracene went into solution which assumed a deep red colour. On allowing to cool the resulting product solidified *en masse*. The solidified mass was treated with more acetic acid and heated on water-bath whereby most of the solids went into solution. The solution was filtered while hot and the filtrate was concentrated to two-third the original volume and at once treated with alcoholic calcium chloride whereby an immediate precipitation occurred. This precipitate was washed successively with water, alcohol, and ether and then dried in a vacuum desiccator. Anthracene mercurichloride is greyish-yellow in colour and melts with decomposition at 181-83°. It is sparingly soluble in benzene and is insoluble in most of the organic solvents; yield 30 per cent. (Found: Hg, 47·57, 48·02; Cl, 8·4. $C_{14}H_9HgCl$ requires Hg, 48·71; Cl, 8·59 per cent.).

Phenanthrene Mercurichloride.—A mixture consisting of phenanthrene (5 g.), mercuric acetate (10 g.) and acetic acid (40 c.c.) was heated in an oil-bath in a pressure flask to a temperature of 120-25° for 4 hours. The resulting yellowish-brown solution was separated from mercurous chloride by filtration. The filtrate was concentrated and allowed to cool and then treated with alcoholic calcium chloride solution. The resulting white precipitate

was separated by filtration and then washed successively with water, alcohol and finally with ether and then dried in vacuum. The compound is a white amorphus powder melting with decomposition at 155-57°. Like the previous mercury compounds it is also insoluble in common organic solvents, yield 40%. (Found: Hg, 47·97, 48·1; Cl, 8·51. $C_{14}H_9HgCl$ requires Hg, 48·71; Cl, 8·59 per cent.).

Fluorene Mercurichloride.—A mixture consisting of fluorene (5 g.), mercuric acetate (12 g.) and acetic acid (35 c.c.) was heated to a temperature of 120-30° for 6-7 hours in a pressure flask. The dissolution of fluorene was gradual and was complete in course of 4-6 hours after which the mixture was heated for two hours more. On allowing to cool a small quantity of unchanged fluorene separated. This was filtered off and the filtrate evaporated to half the original volume and cooled. A white precipitate resulted on the addition of alcoholic calcium chloride solution. The precipitated fluorene mercurichloride was separated, washed repeatedly with water alcohol and ether and then dried in vacuum. The compound melts with decomposition at 130-132° (yield 80%). It is very slightly soluble in acetone and hot acetic acid, is insoluble in all other common organic solvents. (Found: Hg, 49·76; Cl, 8·81. $C_{13}H_9HgCl$ requires Hg, 49·98; Cl, 8·84 per cent.).

Fluorene Mercurihydroxide.—About 50 c.c. of alcohol were taken in a conical flask provided with an upright condenser, and finely powdered fluorene mercurichloride (4 g.) was suspended in it to which moist silver oxide prepared from 2·5 g. of silver nitrate was added. The whole was then heated on a water-bath for 8 hours and then allowed to stand overnight. The alcoholic solution was separated from the silver chloride and silver oxide and other substances by filtration. The filtrate was first concentrated whereby it became turbid due to the separation of some mechanically carried silver salt. This was separated and the filtrate was then evaporated to dryness on a water-bath. The residue thus obtained was of slightly dark colour and was therefore recrystallised from alcohol when a yellowish-white microcrystalline product was obtained. The compound decomposes at 145-47°. It is soluble in water and alcohol but is insoluble in other organic solvents. The aqueous solution is very faintly alkaline to litmus. Its basic character is further proved by its liberation of ammonia from ammonium salts, (yield 10%). (Found: Hg, 51·98. $C_{13}H_9HgOH$ requires Hg, 52·3 per cent.).

Acenaphthene Mercurihydroxide.—Silver nitrate (3 g.) was converted into silver oxide and then washed free of alkali. The moist silver oxide together with 50 c.c. of alcohol and finely powdered acenaphthene mercurichloride (3 g.) was heated under reflux for 14-15 hours on the water-bath. The mass was filtered and the filtrate was concentrated and allowed to cool when a colourless microcrystalline product separated out. The product was dried in a vacuum desiccator. The yield, in this case also, is very small.

The hydroxide is a strong base ; its alcoholic solution turns red litmus blue and it liberates ammonia from ammonium salts and absorbs carbon dioxide from air. It is soluble in alcohol and hot benzene, sparingly in ether, acetone and hot toluene. When heated it shrinks at 175° and melts at 184°. (Found : Hg, 53·95. $C_{14}H_9HgOH$ requires Hg, 54·05 per cent.).

Neither anthracene nor phenanthrene mercurichloride gave any hydroxide derivatives. Analogous treatment resulted in the total disruption of the molecule.

Department of Applied Chemistry,
University College of Science and Technology,
Calcutta.

Received April 30, 1931.

Peroxidases. A New Method of Estimating their Activity.

By Biman Bihari Dey and Mayavaram Vasudeva Sitharaman.

Laccase, obtained from the sap of the lac tree, which was one of the first plant oxidising enzymes to be closely studied (Bertrand, *Compt. rend.*, 1896, **122**, 1215) was shown later to act upon various phenols and to oxidise them to dark quinone-like bodies (Bertrand and Mutermilch, *Ann. Inst. Pasteur*, 1907, **21**, 833). In the course of the series of careful investigations of the oxidising enzymes of such common vegetables as potatoes, beet-root and cabbage, Bach and Chodat (*Ber.*, 1904, **37**, 1842 *et seq.*) succeeded in obtaining fairly pure specimens of these oxidising enzymes, called by them 'peroxidases' because they acted only in the presence of hydrogen peroxide, and elaborated a process for the quantitative estimation of the strengths of such enzyme preparations. It was based on the observation that pyrogallol was oxidised to purpurogallin by a peroxidase in presence of a weak solution of hydrogen peroxide. Willstätter and Stoll (*Annalen*, 1918, **416**, 21; also Willstätter, *Annalen*, 1921, **422**, 47; Willstätter and Pollinger, *Annalen*, 1923, **430**, 269) improved Bach and Chodat's method for the estimation of peroxidases and applied it to the determination of the strength of a particularly pure specimen of this enzyme which they obtained from the horse-radish (*Radicula armoracia*). They also established a convention by which the peroxidase contents of different plants could be measured and compared in terms of their 'peroxidase numbers', *i.e.*, the number of milligrams of purpurogallin obtained from 5 c.c. of the plant sap under certain definite conditions. In the cases of plant saps containing too small a quantity of peroxidase to give a sufficient amount of purpurogallin to form a precipitate by this method, two colorimetric methods have been described, one by Willstätter and Stoll (*loc. cit.*) based on the extraction of the purpurogallin with ether and comparison of its colour with a similar ethereal solution of purpuro-

gallin used as a standard, and the other by Willstätter and Weber (*Annalen*, 1926, **449**, 156) based on the oxidation of leuco-malachite green in dilute acetic acid and sodium acetate solution by the peroxidase in presence of hydrogen peroxide, and comparing the intensity of the colour developed with that of a solution of malachite green used as standard. Recently Wieland and Sutter (*Ber.*, 1928, **61**, 1060), while experimenting with the oxidising enzyme present in a fungus (*Art. lactarius*), found that hydroquinone was auto-oxidised to quinone under the influence of this enzyme, the reaction being assumed to proceed according to the following equation:—

$$C_6H_4(OH)_2 + O_2 = C_6H_4O_2 + H_2O_2$$

The above methods of estimating the strengths of peroxidase preparations are open to several objections, and they can be relied upon as a basis of determining only approximately the relative amounts of oxidising enzymes present in different plants. It has been stated that the enzyme itself undergoes oxidation to some extent and precipitates some insoluble matter along with the purpurogallin, the weight of which thus appears to be greater than it actually is. Again, a certain amount of purpurogallin, which is not quite insoluble in water is lost in the original filtrate and in the washings and is not accounted for. Moreover, according to the method of Willstätter and his co-workers, the reaction is not allowed to proceed to completion but the oxidation is inhibited after a definite interval, usually 10 minutes by the addition of 2*N*-HCl. Apart from the changes caused by the introduction of the acid and its probable solvent action on the purpurogallin (*cf.* Table III) it should be noted that the velocities of oxidation by a peroxidase may differ widely in different plants so that the values obtained by this method may not convey an accurate idea of the relative peroxidase contents of these plants. Thus Rice and Hanzawa (*Ind. Eng. Chem.*, 1922, **14**, 201), who applied this method to the determination of the peroxidase in milk, found that the reaction took seven days to complete, while in the case of an extract of beet-root, the reaction was found by Bach and Chodat (*loc. cit.*) to be completed in less than 24 hours.

In the present paper a method is described which appears to be quite accurate, and should enable a better comparison being made of the peroxidase contents of different plants. It is based on the

interesting observation which was made sometimes ago that when a peroxidase solution containing hydrogen peroxide was treated with an excess of a concentrated aqueous solution of hydroquinone, the latter was quantitatively converted into quinhydrone which separated out as shining needles. It has now been found possible to estimate the quinhydrone formed in this reaction either by a gravimetric or a volumetric process, the latter being preferred both for its simplicity and accuracy.

The experiments described below have been carried out mainly with the common Indian vegetable 'Jhinga' (*Luffa acutangula*, N.O. *Cucurbitaceæ*), and plant saps referred to in various places should be understood to be derived only from this source.

Preparation of Plant Sap.—The fresh fruit, not quite ripe, is cut into thin slices and packed in a stoppered bottle which is placed in a mixture of ice and salt in a glass jar covered with felt and kept at about −8° for 12 hours. The bottle is then opened, the frozen mass transferred to a hand-screw-press (Lautenschlager), the parts of the press coming into direct contact with the sap being made entirely of porcelain. The sap is expressed as completely as possible by applying heavy pressure, an average fruit weighing 250 grams yielding 40-45 c.c. of the sap. The turbid sap is centrifuged (3000 revolution per minute) to free it completely from suspended matter, quickly filtered through glass wool into a 4 oz. stoppered bottle, 3 to 4 drops of toluene are added, and the whole kept in the refrigerator at 0° to 5°. The activity of the enzyme was not found to be appreciably impaired even after a week.

Precipitation of Quinhydrone.—10 C. c. of the clear sap are treated with the same volume of a saturated solution of hydroquinone (4 per cent. approximately), 5 to 10 c.c. of hydrogen peroxide (1 per cent. approximately) are added, and the whole kept in a bath at a temperature of 5° to 10°. During the first ten minutes the liquid remained perfectly clear, and then fine needles of a dark green colour with a bronze-like lustre began to be deposited, the liquid becoming filled with a mass of these crystals at the end of an hour. The crystals were very pure, melted sharply at 171° (correct melting point of quinhydrone is 171°), and gave off the pungent odour of quinone on heating.

Certain interesting results were obtained in the course of the preliminary experiments which were made with a view to obtain standard conditions for the precipitation of quinhydrone by these enzymes.

They showed that any considerable dilution of the reaction mixture with water served to inhibit the oxidation. Thus, on mixing the plant sap (10 c.c.) with freshly boiled water (30 c.c.), and then adding the saturated hydroquinone and 1% hydrogen peroxide solution, and maintaining the whole solution at 10°, no quinhydrone had separated even after 6 hours. On keeping overnight, a small amount of dark precipitate was found to have formed, which, on examination, proved to be mostly insoluble matter mixed with only a small quantity of quinhydrone. Similarly, by varying the amounts of saturated hydroquinone solution, while the volumes of plant sap and H_2O_2 were kept constant, it was found that there was a minimum below which the precipitation of the quinhydrone was incomplete. The results of some of these experiments are shown in Tables I and II.

Estimation of Quinhydrone.—The main objection to gravimetric methods of estimating quinhydrone lies in the difficulty of drying the precipitate. At 100°, it rapidly loses weight due to the volatilisation of the quinone component, and although the weight becomes nearly constant on drying at the laboratory temperature in an evacuated desiccator over sulphuric acid, it takes more than 48 hours for the process to complete. The results which are given in Table III, and which are fairly concordant, were obtained by the following method. The mixture of plant sap (10 c.c.), freshly prepared saturated hydroquinone (10 c.c.) and 1 per cent. hydrogen peroxide (10 c.c.) are kept and stirred in a bath at 10° until the reaction is complete, and no further precipitation takes place (1½ to 2 hours). The whole is then filtered through an Allihn tube fitted with a small perforated disc having a layer of coarse asbestos below and a layer of Gooch asbestos above, to a total height of about 5 mm. The precipitate is washed at first with cold 2% hydroquinone solution and then with ice cold distilled water (5—8 c.c.), the total volume of the wash water as well as that of the reaction mixture being noted for applying a correction for the amount of quinhydrone remaining in solution in the filtrate. For this purpose blank experiments are carried out using the same volumes of plant sap, hydroquinone solution and wash liquid, and a volume of distilled water corresponding to the volume of hydrogen peroxide used. A known weight of quinhydrone in excess of that required to form a saturated solution is now added, the mixture kept at 10° for 1½ to 2 hours, and the quinhydrone filtered, dried and weighed under the same conditions, as before. The difference between the weight of

quinhydrone taken originally and that found after the experiment gives the correction to be applied. After the weight of the Allihn tube has become constant, quinhydrone is disolved out completely with a small amouut of absolute alcohol, and the tube again dried and weighed. In this way, a certain amount of insoluble matter is generally found to have been present which added to the weight of the quinhydrone. The corrections to be applied on account of this insoluble matter are shown in Tables IV and V.

The gravimetric method though not inaccurate involves the application of a number of corrections, and on account of these difficulties, it was later discarded in favour of a volumetric process which gave accurate results in a much shorter time. It is based on the method described by Valeur (*Compt. rend.*, 1899, **129**, 552) which was applied originally to benzoquinone and subsequently to quinhydrone itself by Luther and Leubner (*J. pr. Chem.*, 1912, **85**, 314) in connection with their measurements of the dissociation constant of quinhydrone. The precipitation and filtration of the quinhydrone is carried out in exactly the same way as in the gravimetric method ; the precipitate is then quickly dissolved in alcohol (10 c. c.) and the asbestos in the Allihn tube washed succesively with 3 or 4 portions of 5 c. c. alcohol until the filtrate is colourless. A mixture of alcohol (20 c. c. of 95 per cent.), concentrated hydrochloric acid, (20 c. c.) and potassium iodide solution (20 c.c. of 10 per cent.) is now added to the filtrate contained in a stoppered flask immersed in ice water, and the liberated iodine titrated immediately with decinormal sodium thiosulphate and starch.

The results which are given in Tables IV onwards show remarkable concordance.

TABLE I.

(*Preliminary Experiments*).

Effect of adding varying amounts of freshly boiled distilled water to the mixture of sap, hydroquinone and hydrogen peroxide solutions the volumes of which are kept constant at 10°. It shows that any dilution with water should be avoided.

Vol. of hydroquinone (saturated) = 10 c.c. Vol. of 1% H_2O_2 = 10 c.c. Vol. of sap = 10 c.c.

Expt.	Vol. of water.	Results.
A	50 c.c.	A reddish-brown precipitate small in quantity appears after 24 hours. It is mostly insoluble in alcohol, and liberates very little iodine from KI.

Expt.	Vol. of water.	Results.
B	30 c.c.	Amorphous precipitate formed after six hours; the proportion of quinhydrone is increased.
C	15	Precipitate is crystalline and appears in 2 hours; it is still very impure, and the solid has no sharp melting point.
D	0	Crystals (m.p. 170—71°) appear in 10 minutes and the reaction is completed in an hour.

TABLE II.

Sap A.—The effect of simultaneous variation in the concentration of hydrogen peroxide and hydroquinone on the total yield of quinhydrone. There is a limiting value for the concentration of hydroquinone below which the oxidation appears to be incomplete (*vide* Expts. *g*, *h*, and *i*).

Sap = 10 c.c.

Expt.	Vol. of hydroquinone.	Vol. of H_2O_2.	Time.	Wt. of quinhydrone.
a	12 c.c.	12 c.c.	1½ hours	0·1572 g.
b	10	10	,,	0·1584
c	9	9	,,	0·1554
d	9	9	,,	0·1568
e	9	9	,,	0·1526
f	8	8	,,	0·1534
g	6	6	,,	0·1400
h	5	5	,,	0·1316
i	4	4	18 hours	0·0703

TABLE III.

Sap B.—The effect of adding 2 c.c. 2*N*-HCl for inhibiting the reaction according to Willstätter's method. The yield of the quinhydrone is considerably diminished probably on account of its greater

solubility in a mixture which is approximately 0·05*N*—acid (*vide* Experiments *d* and *e*).

Hydroquinone = 10 c.c. H_2O_2 = 9 c.c. Sap = 10 c.c.

Expt.	Time.	Vol. of 2*N*-HCl added.	Wt. of quinhydrone.
a	1½ hours	nil.	0·1484 g.
b	2 hours.	,,	0·1480
c	,,	,,	0·1460
d	,,	2 c.c.	0·1303
e	,,	,,	0·1295

TABLE IV.

Sap C.—Column 2 shows the correction to be applied for the insoluble matter which is always carried down with the quinhydrone in gravimetric estimations. Experiments *c* and *d* show that the values obtained for the weight of quinhydrone by volumetric methods are greater, when carried out directly, than if it were done after drying the precipitate.

Hydroquinone = 10 c.c. H_2O_2 = 10 c.c. Sap = 10 c.c. Time = 1hr.

	1	2	3	4
Expt.	Wt. of quinhydrone (gravimetric).	Insol. matter.	Corrected weight of quinhydrone.	Wt. of quinhydrone (volumetric).
a	0·2308 g.	0·0026 g.	0·2282 g.	0·2208 g.
b	0·2272	0·0025	0·2247	0·2188
c	—	—	—	0·2215
d	—	—	—	0·2218

TABLE V.

Sap D.—The experiments are the same as in Table IV, excepting that the precipitates were dried at 50° for the gravimetric estimations. The difference, already noticed in Table IV, between the volumetric results when carried out directly, and those obtained after

drying the precipitate, is found to have greatly increased now. It is therefore obviously due to the loss of quinhydrone involved in drying the precipitate which seems to be unavoidable even at the ordinary temperature.

Volumes of hydroquinone, H_2O_2 and sap = 10 c.c. each ; Time = 1 hour.

Expt.	Wt. of Qh. * dried at 50°.	Insol. water.	Corrected wt. of Qh.	Wt. of Qh. (volumetric).	Wt. of quinone corresponding to Qh.
a	0·1738 g.	0·0010 g.	0·1728 g.	0·1715 g.	0·08494 g.
b	0·1734	0·0010	0·1724	0·1703	0·08433
c	—	—	—	0·0778	0·08808
d	—	—	—	0·1768	0·08758

* Qh. = Quinhydrone.

TABLE VI.

Saps F and G.—Column 2 shows the correction to be applied for the amount of quinhydrone held in solution in order to arrive at the absolute weight of this substance formed. The concordance of the results is striking.

Volumes of hydroquinone, H_2O_2 and sap = 10 c.c. each ; Time 1 hour.

(*Sap F*)

	1	2	3	4
Expt.	Wt. of Qh. (volumetric).	Qh. in soln.	True wt. of Qh.	True wt. of quinone.
a	0·1161 g.	0·0215 g.	0·1376 g.	0·06816 g.
b	0·1161	0·0215	0·1376	0·06816
c	0·1162	0·0214	0·1376	0·06816
(*Sap G*)				
d	0·0721	0·0230	0·0951	0·0471
e	0·0721	0·0230	0·0951	0·0471

TABLE VII.

Sap H.—Effect of increasing the concentration of H_2O_2 on the yield of quinhydrone. Enzyme activity appears to diminish with

increasing concentration of this reagent. Willstätter (*Annalen*, 1926, **449**, 154) has made a similar observation in connection with the activity of the peroxidase of beet-root.

Hydroquinone = 10 c.c. Sap = 10 c.c.

Expt.	H_2O_2.	Wt. of Qh.	Correction.	Total wt.	Wt. of quinone corresponding to Qh.
a	10 c.c. (1%)	0·3796 g.	0·0217 g.	0·4013 g.	0·1987 g.
b	,,	0·3781	,,	0·3998	0·1981
c	10 c.c. (2%)	0·2150	,,	0·2367	0·1172
d	,,	0·2150	,,	0·2367	0·1172

TABLE VIII.

Sap I.—A second series of experiments confirming the results set forth in Table VII and leading to the conclusion that the use of a stronger solution of H_2O_2 than 1 per cent. is inadvisable.

Hydroquinone = 10 c.c.; Sap = 10 c.c.; Total vol. = 38 c.c.

Expt.	H_2O_2.	Vol. of wash liquid.	Qh.	Correction.	Total Qh.	Quinone equivalent.
a	10 c.c. (1%)	8 c.c. of 2% Hq. and water.	0·2311 g.	0·0285 g.	0·2596 g.	0·1286 g.
b	,,	,,	0·2313	,,	0·2596	0·1286
c	,, (2%)	,,	0·1161	,,	0·1446	0·07162
d	,, (2%)	,,	0·1163	,,	0·1448	0·07173

Experiments on the estimations of peroxidases in other plant saps and on the preparations of the pure enzymes are in progress.

PRESIDENCY COLLEGE,
MADRAS.

Received July 8, 1931.

The Photo-reduction of Alcoholic Solutions of Ferric Chloride.

By Mata Prasad and N. V. Sohoni.

Ferric salts are reduced when their solutions in aqueous solution of some organic substances or in non-aqueous solvents are exposed to light. The photochemical reduction of the aqueous solutions of ferric chloride has been observed by Benrath (*Annalen*, 1911, **382**, 222) in presence of aldehydes and by Ghosh and Purakayastha (*J. Indian Chem. Soc.*, 1929, **6**, 827) in presence of some organic acids.

Benrath (*J. pr. Chem.*, 1905, **72**,*ii*, 220) has also found that the density of solutions of ferric chloride in methyl and ethyl alcohols changes during exposure to sunlight and to artificial light and from the ratio of the change in density to the time of exposure he has concluded that the reduction of ferric chloride in alcoholic solutions is a photochemical one. Puxeddu and Vodret (*Gazzetta*, 1922, **52**, *i*, 229) have found that the photo-reduction of ferric chloride in ethereal solution follows, up to a certain stage, the equation for monomolecular reactions.

In the following, the photo-reduction of alcoholic solutions of ferric chloride has been studied and the effect of (*a*) intensity of incident light and of small amounts of water, (*b*) temperature and (*c*) neutral electrolytes on the photo-reduction has been examined.

Experimental.

(a) *The Effect of the Intensity of Light and of Small Amounts of Water.*

A 1000-watt Philips lamp was used as the source of light and its intensity was kept constant by means of an adjustable resistance.

Two parallel beams of light obtained from the source were passed through cells containing 4 cm. thick column of distilled water to cut off the heat radiations. The intensity of light of one of the beams was diminished by interposing piles of glass plates in the path of the beam and it was measured by means of a Ruben's thermopile connected to a Broca galvanometer.

The alcohols used were Kahlbaum's or Merck's extra pure chemicals. Ethyl and *n*-amyl alcohols were perfectly anhydrous and *n*-propyl and *n*-butyl alcohols contained traces of water. B. D. H.-A. R. ferric chloride was used.

Solution of ferric chloride was introduced into each of the two identical cells of internal dimensions 20 mm. × 50 mm. The cells were closed by well-fitting rubber stoppers carrying two syphon tubes provided with rubber tubings and pinch-cocks at the outer ends to prevent access of air. The stoppers were made perfectly airtight by coating them with methylated collodion.

The cells were then exposed to light for a certain time at room temperature (29-30°). To ensure optical homogeneity during exposure, the solution was occasionally gently shaken, as done by Ghosh and Purakayastha (*loc. cit.*), and this was found to give reproducible results. Stirring the solution with an inert gas could not be employed, because of the considerable removal of the alcohol caused thereby.

The exposed solution was then transferred to a bottle closed airtight by a rubber cork carrying burettes containing standard solutions of sodium thiosulphate and iodine respectively, so that no air came into contact with the solution. The amount of reduction was determined by adding excess of the thiosulphate solution to the exposed solution and titrating back the excess with the solution of iodine.

The results obtained by this method are comparable amongst themselves. But a maximum difference of 2% was noticed between these results and those obtained, using potassium dichromate in presence of phosphoric acid.

In the following tables, symbols x_1 and x_2 denote the millimoles of ferric chloride reduced, for the intensities I_1 and I_2, respectively, of the light incident on the cells ; the intensities are given in cm. of the galvanometer deflections.

The values of k_1 and k_2, the unimolecular constants for the photo-reduction of ferric chloride, have been calculated wherever possible.

TABLE I.

Solution in Ethyl Alcohol.

$I_1 = 28{\cdot}0$ cm. $I_2 = 5{\cdot}6$ cm.

(*a*) Solution exposed: 2·5 c.c. of 0·174 *M*.

T (hrs.) ...	1	2	3	4	5
$x_1 \times 10^3$ ...	12·17	19·50	24·3$_3$	24·33	22·05
$x_2 \times 10^3$ ...	10·70	19·10	24·13	24·36	24·65

(*b*) Solution exposed: 2·5 c.c. of 0·174 *M* + 0·5 c.c. water.

T (hrs.) ...	½	1	2	3
$x_1 \times 10^3$ ...	17·15	18·40	18·60	16·30
$x_2 \times 10^3$ ...	14·84	21·50	18·90	15·59

(*c*) Solution exposed: 2 5 c.c. of 0·066 *M*.

T (hrs.) ...	2	3	4	5
$x_1 \times 10^3$ ...	2·40	6·80	8·11	10·63
$x_2 \times 10^3$ ...	1·00	3·75	4·65	4·86

(*d*) Solution exposed: 2·5 c.c. of 0.066 *M* + 0·5 c.c. water.

T (hrs.) ...	1	2	3	4	5
$x_2 \times 10^3$ ...	4·10	7·70	8·18	3·40	4·00
$k_2 \times 10^3$ ...	4·76	5·24	3·80		

TABLE II.

Solution in n-*Propyl Alcohol.*

$I_1 = 28{\cdot}0$ cm. $I_2 = 9{\cdot}0$ cm.

(*a*) Solution exposed: 2·5 c.c. of 0·176 *M*.

T (hrs.) ...	1	2	3	4	5
$x_1 \times 10^3$ ...	27·60	26·80	23·70	22·55	20·00
$x_2 \times 10^3$ ...	23·80	26·20	25·50	22·80	22·30

(*b*) Solution exposed: 2·5 c.c. of 0·088 *M*.

T (hrs.) ...	1	2	3	4
$x_1 \times 10^3$ ...	13·70	15·50	14·50	15·35
$x_2 \times 10^3$ ...	6·40	12·68	12·10	11·30

$k_1 = 0{\cdot}0132$; $k_2 = 0{\cdot}0064$.

TABLE III.

Solution in n-Butyl Alcohol.

$I_1 = 24$ cm. $I_2 = 5{\cdot}9$ cm.

(*a*) Solution exposed: 2·5 c.c. of 0·14 *M*.

T (hrs.)	...	½	1	1½	2	3
$x_1 \times 10^2$	...	5·96	12·80	11·70	9·75	8·10
$x_2 \times 10^2$	...	4·50	13·80	11·06	9·40	7·80

(*b*) Solution exposed: 2·5 c.c. of 0·0672 *M*.

T (hrs.)	...	1	1½	2	3
$x_1 \times 10^2$	...	4·75	6·50	7·30	11·05
$x_2 \times 10^2$	...	1·15	2·42	4·20	6 63

TABLE IV.

Solution in n-Amyl Alcohol.

$I_1 = 22{\cdot}45$ cm. $I_2 = 14{\cdot}75$ cm.

(*a*) Solution exposed: 2·5 c.c. of 0·236 *M*.

T (hrs.)	...	1	2	3	4	5	6
$x_2 \times 10^2$	...	10·50	15·56	27·88	36·22	40·87	44·16
$k_2 \times 10^3$	...	3·27	3·39	3 55	3·97	3·93	3·83

Mean 3·66

(*b*) Solution exposed: 2·5 c.c. of 0·236 *M* + 0·5 c.c. water.

T (hrs.)	...	1	1½	2	3	4
$x_1 \times 10^2$	...	24·00	—	37·23	36·50	33·42
$x_2 \times 10^2$	...	21·13	31·44	44·31	37·36	27·65

(*c*) Solution exposed: 2·5 c.c. of 0·0637 *M*.

T (hrs.)	...	1	2	3	4	5
$x_1 \times 10^2$	...	8·72	10·58	6·15	6·60	6·07
$x_2 \times 10^2$	...	6·87	7·50	7·00	5·47	4·12

$k_1 = 0{\cdot}0112$; $k_2 = 0{\cdot}0069$.

It will be seen that the intensity of the incident radiation has less effect on the velocity of the photo reduction of concentrated solutions of ferric chloride than on the weaker ones.

By plotting the values of x and T, it will be seen that something like a stationary state is reached in the photo-reduction of solutions of ferric chloride in anhydrous alcohols; the equilibrium is set up earlier in the concentrated solutions than in the dilute ones. The addition of water both to the concentrated and to the dilute solutions accelerates the reduction of ferric chloride in the beginning but with the progress of the reaction, apparently the reverse reaction is more accelerated than the direct one. This is indicated by a maximum point in the (x, T) curves for this solutions. A complete reversal, however, never takes place.

Van Alphen (*Rec. trav. chim.*, 1930, **49**, 754) has found that when a solution of ferric chloride in ethyl alcohol is heated in sealed tubes at 160° under high pressure, a reversible thermal reaction takes place. The reaction is accelerated when hydrated ferric chloride is used but the addition of larger amount of water retards the reaction.

The reduction of ferric chloride is almost zero-molecular in the concentrated solutions but it tends to become unimolecular in the weaker ones, especially in presence of water. The order of the reaction depends both upon the concentration of the solution and upon the intensity of the incident light.

(b) *The Effect of Temperature.*—Temperature coefficients of alcoholic solutions of ferric chloride for 10° rise were measured between 30° and 40°. A glass-fronted air thermostat was used and the temperature was kept constant within $\pm 0{\cdot}2°$. The reaction cell was properly screened from the bulb heater and the same arrangement of light was used as described previously. The results obtained are given in the following tables in which x_{30} and x_{40} represent millimoles of ferric chloride reduced at the temperatures 30° and 40° respectively and r, the temperature coefficient for 10° rise, *i.e.*, the ratio of $x_{40} : x_{30}$.

TABLE V.

Solution in Methyl Alcohol.

Conc. of $FeCl_3 = 0{\cdot}08084$ *M.*				Conc. of $FeCl_3 = 0{\cdot}1992$ *M.*			
T (hrs.).	$x_{40} \times 10^3$.	$x_{30} \times 10^3$.	r.	T (hrs.).	$x_{30} \times 10^3$.	$x_{30} \times 10^3$.	r.
1	3·31	3·05	1·085	1	4·6	4·1	1·122
2	—	4·00	—	2	8·0	7·1	1·127
3	4·78	4·82	0·992	3	8·4	4·9	1·063
		Mean	1·0385			Mean	1·104

TABLE VI.

Solution in Ethyl Alcohol.

Conc. of $FeCl_3$ = 0·1008 *M*.				Conc. of $FeCl_3$ = 0·192 *M*.			
T (hrs.).	$x_{40} \times 10^3$.	$x_{30} \times 10^3$.	*r*.	*T* (hrs.).	$x_{40} \times 10^3$.	$x_{30} \times 10^3$.	*r*.
1	2·0	2·0	1·00	1	5·80	4·4	1·318
2	2·5	2·6	1·00	2	6·32	6 4	0·986
3	3·07	3·1	1·00	3	8·19	8·0	1·125
			Mean 1·00				Mean 1·143

TABLE VII.

Solution in n-*Propyl Alcohol.*

Conc. of $FeCl_3$ = 0·092 *M*.				Conc. of $FeCl_3$ = 0·1772 *M*.			
T (hrs.).	$x_{40} \times 10^3$.	$x_{30} \times 10^3$.	*r*.	*T* (hrs.).	$x_{40} \times 10^3$.	$x_{36} \times x10^3$.	*r*.
1	1·60	1·80	0·888	1	1·91	1·45	1·317
2	2·01	2·05	0·980	2	1·55	1·50	1·033
3	2·30	2·33	0·978	3	2·20	2·00	1·100
			Mean 0·948				Mean 1·150

TABLE VIII.

Solution in n-*Butyl Alcohol.*

Conc. of $FeCl_3$ = 0·0824 *M*.				Conc. of $FeCl_3$ = 0·225 *M*.			
T (hrs.).	$x_{40} \times 10^3$.	$x_{30} \times 10^3$	*r*.	*T* (hrs.).	$x_{40} \times 10^3$.	$x_{30} \times 10^3$.	*r*.
1	0·95	1·00	0·95	½	4·45	4·40	1·010
2	1·48	1·32	1·12	1	9·22	8·9	1·036
3	2·10	2·10	1·00	1½	12·50	12·90	0·969
			Mean 1·023	2	—	17·63	—
							Mean 1·005

The temperature coefficients of the photo-reduction of ferric chloride in alcoholic solutions for 10° rise are between 1·0 and 1·15 and they appear to be little affected by the change in the concentration of the solutions. This value of the temperature coefficient is nearly the same as that (1·01) obtained by Berthelot (*Compt. rend.*, 1915, **160**, 440) for the reduction of ferric chloride by oxalic acid

The temperature coefficient for a number of photochemical halogen, reactions has been found by a number of workers to be greater than unity. But in the majority of the photochemical reactions involving the decomposition of a molecule containing a

halogen, the temperature coefficient is nearly unity. Thus the temperature coefficients of the decomposition of hydrogen iodide (Bodenstein and Lieneweg, *Z. Phys. Chem.*, 1926, **119**, 123), of NOCl (Kiss, *Rec. trav. chim.*, 1923, **42**, 665), of NH_3 (Kühn, *compt. rend.*, 1924, **178**, 708) and of Cl_2O (Bodenstein and Kistiakovsky, *Z. Phys. Chem.*, 1925, **116**, 371) were found to be nearly unity. In view of these data, it may be inferred that the primary reaction in the photo-reduction of ferric chloride in alcoholic solutions is the breaking up of the ferric chloride molecules into those of ferrous chloride and chlorine.

(c) *The Effect of Neutral Electrolytes.*—To study the effect of electrolytes, different volumes of known solutions of the electrolytes in alcohols were added to the same volume of the alcoholic solutions of ferric chloride and the total volume of the mixture was made the same in each case. The concentrations of the electrolytes were small enough not to introduce any appreciable alteration in the absorption of light. The results obtained are given in the following tables, in which E represents the equivalents of the electrolytes present in one litre of the reaction mixture and x, millimoles of ferric chloride reduced. The period of exposure of solutions was one hour in all cases and the intensity of light falling on the solution was kept at the same value during each exposure.

TABLE IX.

0·1868*M*-$FeCl_3$ *solution in Methyl Alcohol.*
With no electrolyte, $x \times 10^2 = 4{\cdot}50$.

Electrolyte.	E.	$x \times 10^2$.	% Velocity of reaction
NaCl	0·017	2·46	54·67
	0·034	1·10	24·45
	0·051	0·43	9·56
KCl	0·005	2·25	50·00
	0·010	0·90	20·00
	0·015	0·30	6·66
LiCl	0·050	2·90	64·45
	0·100	0·00	0·00
$MgCl_2$	0·017	2·10	46·66
	0·034	0·00	0·00

TABLE X.

0·305 *M*-$FeCl_3$ *solution in Ethyl Alcohol.*
With no electrolyte, $x \times 10^2 = 14{\cdot}2$.

Electrolyte.	E.	$x \times 10^2$	% Velocity of reaction.
NaCl	0·0255	13·10	92·23
	0·034	12·20	85·91
KCl	0·005	12·90	90·84
	0·010	12·31	86·68
LiCl	0·050	13·26	93·38
	0·100	12·40	87·33
$MgCl_2$	0·017	13·10	92·23
	0·034	12·40	87·33

TABLE XII.

0.211 *M*-$FeCl_3$ *solution in* n-*Propyl Alcohol.*

With no electrolyte, $x \times 10^2 = 5{\cdot}42$.

Electrolyte.	*E.*	$x \times 10^2$.	% Velocity of reaction.
NaCl	0·017	3·47	64·02
	0·034	2·32	42·80
KCl	0·005	4·12	76·03
	0·010	3·78	69·74
LiCl	0·050	3·12	57·56
	0·100	1·92	35·42
$MgCl_2$	0·017	4·32	79·70
	0·034	4·42	81·55

TABLE XI.

0.115 *M*-$FeCl_3$ *solution in* n-*Butyl Alcohol.*

With no electrolyte, $x \times 10^2 = 1{\cdot}16$.

Electrolyte.	*E.*	$x \times 10^4$.	% Velocity of reaction.
NaCl	0·017	0·55	47·41
	0·034	0·60	51·72
KCl	0·005	0·90	77·50
	0·075	0·50	43·10
LiCl	0·050	0·67	57·75
	0·075	0·40	34 47
$MgCl_2$	0·017	0·46	39·60
	0·034	0·26	22 41

The results indicate that the photo-reduction of ferric chloride is inhibited by the addition of small quantities of the electrolytes and the inhibition is greater, the larger the amount of the electrolyte added.

Berger (*Rec. trav. chim.*, 1921, **40**, 387; *ibid.*, 1925, **44**, 47) has found that neutral electrolytes have a catalytic effect on many photochemical reactions and it is primarily brought about by a change in the electrostatic forces within the solution. On the basis of the effect of electrolytes, he has classified the photochemical reactions into three groups: (*i*) those that are very sensitive to the presence of electrolytes, (*ii*) those in which the inhibition, noticeable at low concentrations, becomes pronounced at higher concentrations, and (*iii*) those in which even the highest concentration of electrolytes do not affect the velocity of reaction by more than a few per cent.

The photo-reduction of ferric chloride in alcoholic solutions probably belongs to the second group of reactions.

Summary.

1. The intensity of incident light has less effect on the velocity of photo-reduction of the comparatively concentrated solutions than on the dilute ones.

2. The reaction appears to reach a stationary state in solutions in perfectly anhydrous alcohols.

3. The addition of water accelerates the direct reaction for sometime but afterwards the reverse reaction is more accelerated than the direct one.

4. The temperature coeffecients for 10° rise between 30° and 40° lie between 1·00 and 1·15.

5. The addition of minute quantities of sodium chloride, lithium chloride and magnesium chloride has an inhibitive effect.

THE CHEMICAL LABORATORIES,
THE ROYAL INSTITUTE OF SCIENCE,
BOMBAY.

Received April 4, 1931.

Ultra-violet Absorption in the Mixtures of Chromates and Dichromates.

By Nanasaheb Ramji Tawde.

Some results on the extinction coefficients of the mixtures of chromates and dichromates have recently been reported and the data have been utilised to determine the percentage composition of such mixtures (Paranjpe and Tawde, *Indian J. Phys.*, 1929-30, **6**, 533). The above procedure is applicable only to concentrated solutions, as no absorption in the visible region is given by weak solutions of these mixtures.

Selective absorption is given by these solutions in the ultra-violet region. Hantzsch, (*Z. Phys. Chem.*, 1910 72, 362) formulated definite absorption curve for dichromate and chromate. The peak of the chromate curve lies in the same wave-length region as that of dichromate. This holds also for the minima of the curves. There is one band in the solution of dichromate and two bands in that of chromate. As chromate is changed gradually into dichromate by the addition of acid, its second band begins to disappear. This observation has been utilised to obtain a quantitative estimate of the percentage composition of the mixture.

Experimental.

For these experiments, a solution of a single salt or of two salts will be called normal when it contains one gram-atom (52 g.) of chromium in a litre of solution.

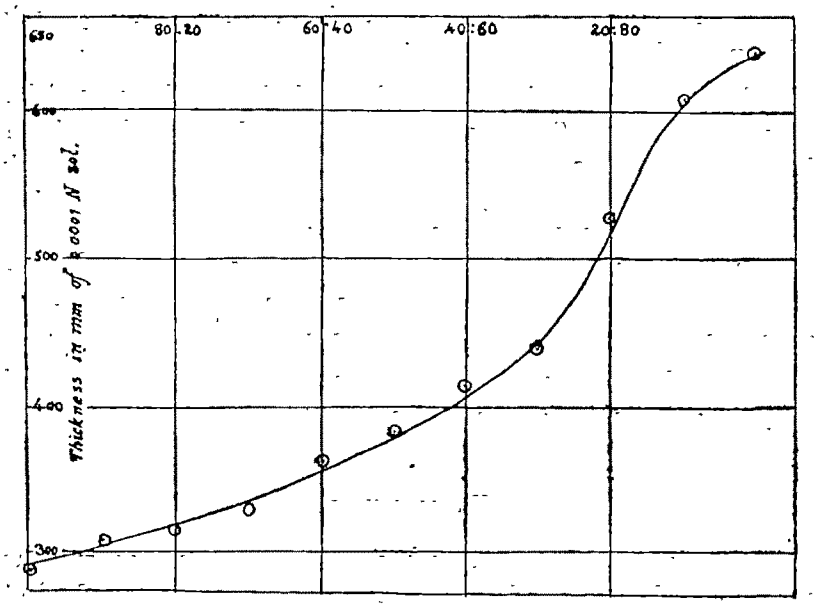
The spectrograph used was R. Fuess quartz prism instrument recording a region from 5200 Å to 2100 Å. The source of light used was an iron arc. The main difficulty is that the feeble lines disappear altogether, while the stronger ones persist through the band. In such cases the observations were confirmed by using a carbon arc.

The experiments were made under uniform conditions at room temperature.

Results.

The peak (transmission band) of both chromate and dichromate and their mixtures was found to be at 3140Å. The dispersion of the spectrograph in this region was 14Å per mm. By trial photographs the thickness and concentration of solution in Baly's tube were so adjusted that the layer just began to absorb light in this wavelength. This thickness when reduced to *N*-10,000 basis for any solution represents the height of its transmission peak. The results are given in figures 1 and 2 below.

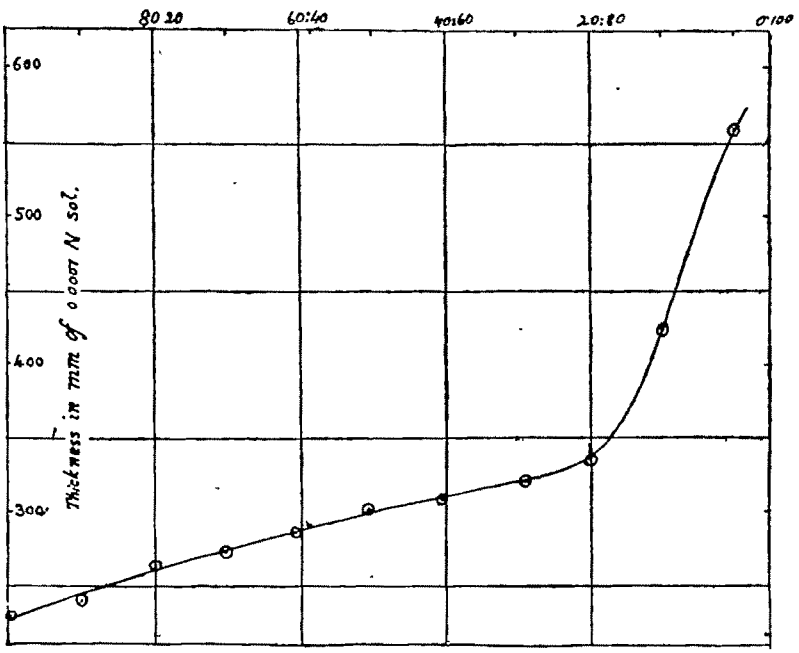
Fig. 1.



$K_2Cr_2O_7$: K_2CrO_4

The percentage compositions of mixtures of chromate and dichromate as estimated by the above curves were compared as in the previous paper (*loc. cit.*) with the values obtained by the chemical method(Sacher, *Farbenzeit*, 1916, **22**, 213). The agreement is fairly satisfactory and similar to that reported previously.

Fig. 2.



$Na_2Cr_2O_7 : Na_2CrO_4$

Summary.

The estimation of chromate in presence of dichromate reported in a previous paper, has been extended to more dilute solutions.

The author wishes to express his thanks to Prof. Paranjpe for his continued interest and encouragement during the progress of the work.

PHYSICS LABORATORIES,
ROYAL INSTITUTE OF SCIENCE,
MAYO ROAD, BOMBAY.

Received December 15, 1930.

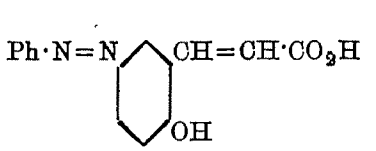
The Effect of Lactonic Ring on the Colour of Azo-dyes.

By Dukkhaharan Chakravarti.

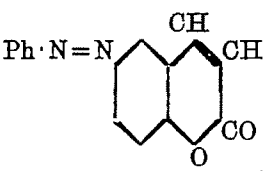
Sen and Chakravarti (*J. Amer. Chem. Soc.*, 1928, **50**, 2428) prepared some azo-methine, pyronine and triphenylmethane dyes containing a lactonic ring and discussed the influence of the lactone. In order to study the auxochromic or the hypsochromic effect of a lactonic ring, a series of azo-dyes with a lactone ring has now been prepared.

The azo-dyes studied have been prepared in two different ways: *viz.*, by diazotising aryl amines and coupling them with coumarin in an alkaline solution (*cf.* Borsche, *Ber.*, 1904, **37**, 4116; Hewitt and Mitchell, *J. Chem. Soc.*, 1905, **87**, 1229; 1906, **89**, 15; 1906, **89**, 17), and by diazotising 6-aminocoumarin and coupling it with different phenols and also with various coumarin derivatives in an alkaline solution.

For a comparative study, the benzene- and naphthalene-azo-coumarins and the benzene- and naphthalene-azocoumaric acids (for preparation of these compounds see Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 391) have been very useful. It has been found that in the azo-coumaric acid derivatives, the affinities of the compounds for the fibres are much greater than those of the azo-coumarin derivatives.



Benzeneazo-o-coumaric acid.



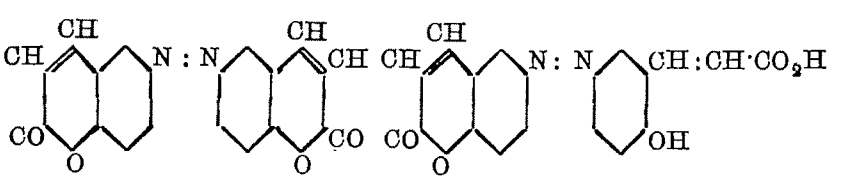
Benzeneazocoumarin.

This shows that the auxochromic effect of the free hydroxyl group in the coumaric acid derivatives appreciably diminishes in the coumarin derivatives, where the hydroxyl group is masked, so to say, by the closure of the lactone ring. Although the dyeing properties of the lactones are much less, it is noteworthy that the

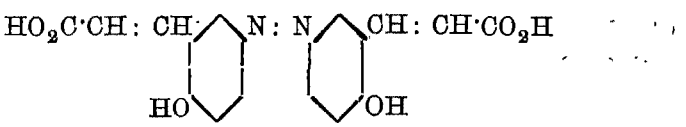
depth of colour of the lactone and the corresponding *ortho*-coumaric acid is much the same ; the lactonic ring behaving in this respect just like a hydroxyl group. The following table compares the properties of these two series of compounds.

Name.	Colour.	Shade on silk and wool.	Name.	Colour.	Shade on silk and wool.
1. Benzeneazo-coumarin.	Brownish-yellow	Light yellow	1. Benzene-azo-*o*-coumaric acid	Yellow	Bright yellow.
2. *m*-Nitro-benzeneazo-coumarin.	Brownish-yellow	Pale yellow	2. *m*-Nito-benzeneazo-*o*-coumaric acid.	Deep yellow	Brilliant yellow
3. *o*-Nitro-benzeneazo-coumarin.	Yellow	Dull yellow	3. *o*-Nitroben-zeneazo-*o*-coumaric acid	Reddish-yellow	Yellow
4. *p*-Nitro-benzeneazo coumarin.	Red	Pale yellow	4. *p*-Nitro-benzeneazo-*o*-coumaric acid	Brick red.	Yellowish-red
5. Diphenyl-bis-azo-di-coumarin.	Yellow	Yellow	5. Diphenyl-bisazodi-*o*-coumaric acid	Yellow	Yellow with slight orange tinge
6. Naphthalene-*α*-azocoumarin.	Brown	Yellow	6. Naphthalene-*α*-azocoumaric acid	Greenish-yellow	Bright yellow
7. Naphthalene-*β*-azocoumarin.	Yellow	Slightly yellowish tinge	7. Naphthalene-*β*-azocoumaric acid.	Yellow	Yellow
8. Benzene-azo-4 : 6-di-methylcoumarin	Orange	Very faint yellowish tinge	8. Benzeneazo-*β* : 5-dimethyl-*o*-coumaric acid.	Chocolate	Yellow

The influence of the lactonic ring on the depth of colour and dyeing property is shown clearly by a comparative study of the following three compounds:—(1) Azocoumarin (2) coumarinazo-coumaric acid, (3) azocoumaric acid. (*cf.* Sen and Chakravarti, *J. Indian Chem. Soc.*, 1930, 7, 247).



Azocoumarin. Coumarinazo-*o*-coumaric acid.



Azo-o-coumaric acid.

Of these azocoumaric acid (reddish-brown), in which two hydroxyl groups exert auxochromic effect, dyes reddish-brown shade, the coumarinazocoumaric acid (light brown) containing one lactonic ring and one hydroxyl group a yellow shade and azocoumarin, in which there are two lactonic rings, produces a faint yellowish tinge on the fibres. When dissolved in caustic alkali all of them give a red solution.

Dimethylazocoumarins, though they contain two lactonic rings have little affinity for the fibres, coumarinazo-4:6-dimethylcoumarin (golden yellow) and coumarinazo-4:7-dimethylcoumarin (greenish-yellow) producing only a dull yellow tinge on silk. It has not been possible to break up the lactones and isolate the free acids in these cases for the sake of comparison.

Coumarinazo-4-methyl-α-naphthacoumarin (orange) produces an orange shade on silk and wool probably due to the presence of the naphthalene nucleus.

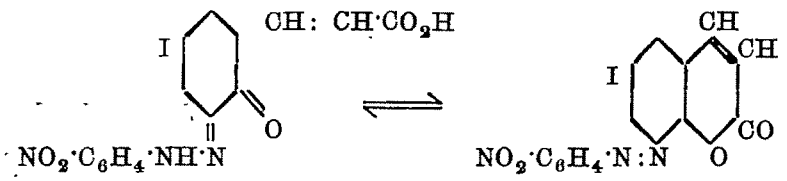
By introducing an additional hydroxyl group into the azocoumarin molecule as in coumarinazo-7-hydroxy-4-methylcoumarin, the colour of the compound deepens to red and the shades on silk and wool are also deepened to reddish-brown. This compound is very similar in colour to coumarinazoresorcinol (red) which also produces a red shade on silk and wool.

Coumarinazo-7:8-dihydroxy-4-methylcoumarin (grey) have a polygenetic property producing different shades on mordanted wool.

Coumarinazodimethylaniline produces a faint yellow colour in alkaline solution and a violet colour in acid solution, the sharp change of colour being very suitable for an indicator.

It is interesting to note that 6-iodocoumarin and 6-aldehydocoumarin couples with a diazotised amine to form a free acid and not a lactone. In these cases coupling takes place in the 8-position and it is probable that the acids isolated are the quinonoid forms of the *o*-hydroxyazocompounds according to the hypothesis of Hewitt

(*J. Chem. Soc.*, 1905, 87, 225). Thus diazotised, *p*-nitoaniline forms with 6-iodocoumarin, the free acid, thus:



It is always noticed that the yield of the azo-compounds is not satisfactory when the coupling takes place in the 8-position. Incidentally it may also be mentioned that 6-nitrocoumarin does not form an azo-dye due to the inhibiting action of the nitro-group and that attempts to couple diazotised aminocoumarin with an alkaline solution of aminocoumarin itself are unsuccessful.

Experimental.

Modified Method for the Preparation of 6-Aminocoumarin.—Morgan and Micklethwaits' method (*J. Chem. Soc.*, 1904, 85, 1230) has been found to give poor yields. It has been modified as follows: 6-Nitrocoumarin (10 g.) (readily obtained in a very pure form melting at 185° by crystallising from a small quantity of pyridine) is dissolved in boiling rectified spirit (250 c.c.) in a 500 c.c. flask with an upright condenser and iron filings (20 g.) are added to it. Concentrated hydrochloric acid (20 c.c.) is slowly added drop by drop to the boiling alcoholic solution with occasional shaking and the heating continued for about two hours. The alcohol is then distilled off and the solution, diluted with water acidified with hydrochloric acid, is filtered off from the unchanged iron filings and nitrocoumarin, and made alkaline with sodium bicarbonate, when a voluminous greenish-yellow precipitate separates out. The precipitate is collected and crystallised from a large volume of boiling water, when long yellow needles separate out. By this method about 7 g. of pure 6-aminocoumarin, m.p. 167° are obtained.

Azocoumarin.—6-Aminocoumarin (2 g.) is dissolved in sulphuric acid (5 c.c. conc. sulphuric acid in 50 c.c. water) and a solution of sodium nitrite (1 g. in 6 c.c. water) is added all at once to prevent the formation of diazoamino compound.

The diazotised solution is then added to an alkaline solution of coumarin (1·8 g.) and after keeping overnight, the solution is acidified with hydrochloric acid and the precipitate dried and crystallised from nitrobenzene or a mixture of nitrobenzene and pyridine (3:1) in beautiful yellow needles which do not melt up to 300°. It dissolves in caustic alkalis and in concentrated sulphuric acid with a red solution. It is almost insoluble in the ordinary organic solvents. (Found: N, 8·5. $C_{18}H_{10}O_4N_2$ requires N, 8·8 per cent.).

Coumarinazo-o-coumaric acid is prepared by coupling diazotised 6-aminocoumarin with an alkaline solution of *o*-coumaric acid in the usual manner. It is purified by desolving in sodium carbnnate, reprecipitating with acid and finallp crystallising from boiling rectified spirit. It is a light-brown substance decomposing at 177° and its solutions in caustic alkalis and in concentrated sulphuric acid are red in colour. Its colour changes to red when in contact with hydrochloric acid. (Found: N, 8·1. $C_{18}H_{12}O_5N_2$ requires N, 8·3 per cent.).

Azo-o-coumaric Acid.—A solution of azocoumarin (1 g.) in caustic potash (1 g. in 10 c.c. water) is diluted with water (150 c.c.) and boiled for about an hour with powdered yellow mercuric oxide (2 g.) (*cf.* Sen and Chakravarti, *J. Indian Chem. Soc.*, 1930, 7, 247). The cold solution, filtered from the mercuric oxide, is acidified with hydrochloric acid and the precipitate dissolved in ammonia. The ammoniacal solution is acidified and the precipitate dried and crystallised from dilute alcohol in reddish-brown needles, which do not melt up to 300°. It dissolves in caustic alkalis forming a dull red solution and in concentrated sulphuric acid with a deep red solution. Its colour changes to light violet with the addition of hydrochloric acid. (Found: N, 7·6. $C_{18}H_{14}O_6N_2$ requires N, 7·9 per cent.).

Coumarinazo-4:7-dimethylcoumarin prepared by coupling diazotised 6-aminocoumarin with an alkaline solution of 4:7-dimethylcoumarin, is obtained as a microcrystalline greenish-yellow substance from nitrobenzene, melting at 280°. It is insoluble in the ordinary organic solvents and dissolves in caustic alkalis and in concentrated sulphuric acid with a red solution. (Found: N, 8·3. $C_{20}H_{14}O_4N_2$ requires N, 8·09 per cent.).

Coumarinazo-4:6-dimethylcoumarin obtained by coupling diazotised aminocoumarin with an alkaline solution of 4:6-dimethylcoumarin, crystallises as golden-yellow needles from pyridine, m.p. 262°. It is insoluble in the ordinary organic solvents and forms a

deep red solution in caustic alkalis and in concentrated sulphuric acid. (Found: N, 8·1. $C_{20}H_{14}O_4N_2$ requires N, 8·09 per cent.).

Coumarinazo-4-methyl-α-naphthacoumarin prepared by coupling diazotised 6-aminocoumarin with an alkaline solution of α-naphthamethylcoumarin, crystallises in orange needles which do not melt up to 280°, from a large volume of pyridine. It dissolves in caustic alkalis and in concentrated sulphuric acid forming a deep violet solution. It is insoluble in the ordinary organic solvents. (Found: N, 7·73. $C_{23}H_{14}O_4N_2$ requires N, 7·33 per cent.).

Coumarinazo-7-hydroxy-4-methylcoumarin prepared by coupling diazotised 6-aminocoumarin with an alkaline solution of β-methylumbelliferone, is a microcrystalline powder from glacial acetic acid, softening at 205°. It dissolves in caustic alkalis and in concentrated sulphuric acid forming a deep red solution. (Found: N, 8·31. $C_{16}H_{12}O_5N_2$ requires N, 8·04 per cent.).

Coumarinazo-7:8-dihydroxy 4-methylcoumarin is prepared by coupling diazotised 6-aminocoumarin with an alkaline solution of β-methyldaphnetin. The deep red solution, on acidification with hydrochloric acid, gives a brownish black precipitate, which is dried in the vacuum desiccator, dissolved in pyridine and poured into toluene. It is a grey substance softening at 282°. It dissolves in caustic alkalis and in concentrated sulphuric acid forming a dark red solution. (Found: N, 7·4. $C_{19}H_{12}O_6N_2$ requires N, 7·7 per cent.).

Coumarinazoresorcinol is prepared from diazotised 6-aminocoumarin and resorcinol. It is a reddish-brown substance melting at 245°, dissolving in caustic alkalis and in concentrated sulphuric acid with a deep red colour. (Found: N, 9·8. $C_{15}H_{10}O_4N_2$ requires N, 9·92 per cent.).

Coumarinazodimethylaniline.—Dimethylaniline (1·5 g.) in hydrochloric acid solution is slowly added to diazotised solution of 6-aminocoumarin (2 g.) and the solution on keeping overnight is made alkaline with ammonia and distilled in steam. The precipitate is filtered off, dissolved in alcohol and poured into water. It is finally crystallised in beautiful plates melting at 231° from absolute alcohol containing a few drops of nitrobenzene. It is a reddish-yellow substance soluble in alkalis with a yellow colour and in acids with a violet colour. It seems to be a good indicator, the change of colour being very sharp. (Found: N, 14·55. $C_{17}H_{15}O_2N_3$ requires N, 14·3 per cent.)

The Azo-compound of p-*Nitroaniline with 6-Iodocoumarin.*—It is obtained by coupling diazotised *p*-nitroaniline with an alkaline

solution of 6-iodocoumarin. It is purified by dissolving in ammonia and precipitating with acetic acid. A reddish-brown solid freely soluble in sodium carbonate and bicarbonate solutions. (Found: N, 9·9. $C_{15}H_{10}O_5N_3I$ requires N, 9·57 per cent.).

The *azo-compound* of 6-aminocoumarin with 6-iodocoumarin is purified by dissolving in sodium bicarbonate and reprecipitating with acetic acid. The solution and precipitation are repeated several times and the precipitate dried, dissolved in alcohol and poured into water. Brown powder, freely soluble in sodium bicarbonate solution with effervescence. (Found: N, 5·88. $C_{18}H_{11}O_5N_2I$ requires N, 6·06 per cent.).

The *azo-compound* of 6-aminocoumarin with 6-aldehydocoumarin is prepared in the usual manner and purified by dissolving in ammonia and reprecipitating with acetic acid. It is a brown powder insoluble in alcohol and soluble in sodium bicarbonate. (Found: N, 7·2. $C_{19}H_{12}O_6N_2$ requires N, 7·7 per cent.).

p-*Nitrobenzeneazo*-7:8-*dihydroxy*-4-*methylcoumarin* is prepared by coupling diazotised *p*-nitroaniline with an alkaline solution of β-methyldaphnetin. It is obtained in the pure state as a reddish-brown powder softening at 292° by pouring its solution in pyridine into toluene. (Found: N, 12·02. $C_{16}H_{11}O_6N_3$ requires N, 12·3 per cent.).

The author's best thanks are due to Prof. R. N. Sen for the kind interest he has taken in this investigation.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.

Received June 29, 1931

Decomposition of Phenol and Naphthol Ethers by means of Concentrated Hydrochloric Acid.

By G. B. Kolhatkar and R. P. Ghaswalla.

Ethers decompose to some extent when heated with halogen acids. Hydriodic acid at its boiling point decomposes most ethers. Concentrated hydrobromic acid also decomposes ethers to a considerable extent at a high temperature (Stoermer, *Ber.*, 1908, **41**, 321; Kolhatkar, *J. Indian Inst. Sci.*, 1918, **2**, 179) found that anisole and phenetole undergo slight decomposition with 19 per cent. hydrochloric acid in a sealed tube at 100°.

The present investigation was undertaken to study the influence of different substituent groups in the benzene ring on the decomposition of phenolic ethers when heated in sealed tubes with concentrated hydrochloric acid. The following ethers were used in the investigation —anisole, phenetole, *ortho-*, *meta-* and *para-*(nitro-, chloro-, bromo-, amino-, methyl- and acetyl-). anisoles, *p*-chloro- *p*-bromo- and *p*-nitro-phenetoles ; 2:4:6 tribromoanisole ; 2:4- and 2:6-dinitroanisoles ; methyl ethers of α- and β- naphthol and methyl ether of aromatic tetrahydro-α-naphthol.

The solid ethers were carefully purified by crystallisation and the liquid ethers by fractional distillation. Mixtures of ethers and concentrated hydrochloric acid were introduced in hard glass tubes (1 cm. dia. and 25 cm. length). The tubes were sealed and kept in a bomb furnace for two hours at 180°.

Preliminary experiments were carried out to study the action of concentrated hydrochloric acid on aromatic ethers. Aromatic ethers were heated with concentrated hydrochloric acid in sealed tubes at 180° for some hours. The reaction mixture was then made alkaline, and the undecomposed aromatic ether was extracted with ether and its weight was determined. The alkaline solution (after extraction with ether) was made acidic and the liberated phenol was extracted with ether and its weight was also determined. This weight was found equal to that calculated on the assumption that in the

action of hydrochloric acid on aromatic ethers only phenols are formed. The liberated phenol was also identified by appropriate tests.

The decomposition which the ethers suffered was determined in most cases by estimating the liberated phenols. A mixture of potassium bromide and potassium bromate, in presence of concentrated hydrochloric acid, brominates readily a large number of phenols and the amount of bromine taken up is usually quite definite. *p*-Nitroanisole, and *p*-nitrophenetole did not react with bromine. The phenols in these cases were estimated by the bromination method in presence of the ethers. In other cases, as the ethers react to a certain extent with bromine, the undecomposed ethers were first extracted in an alkaline solution by ether. The phenols were then estimated. In the case of *m*-bromophenol, 2:4:6-tribromophenol and the three aminophenols, the bromination method does not give good results. The undecomposed ether in these cases was directly estimated after separation from the phenol by extraction with ether in a strongly alkaline solution.

Experimental.

Experiments to show that bromate-bromide mixture can be satisfactorily used for estimating phenol, alone and when mixed with anisole. 1 C. c. of bromate-bromide mixture liberated 0·0192 g. of bromine.

Estimation of Phenol.

Phenol	Bromate-bromide mixture added.	0·1*N*-$Na_2S_2O_3$ for back titration	Bromine used up.	Calculated amount of bromine.
0·10 g.	30 c.c.	8·3 c.c.	0·5096 g.	0·5106 g.
0·05	20	60·2	0·2544	0·2553
0·04	20	22·5	0·2024	0·2040
0·02	10	11·3	0·1016	0·1020
0·01	10	177·	0·0504	0·05106

One molecule of phenol uses up 3 molecules of bromine.

Estimation of Phenol in a Mixture of Phenol and Anisole.

Since anisole reacts with bromine, the former was removed by extraction in an alkaline mixture by ether and the phenol estimated as before.

Phenol.	Anisole added.	Bromate-bromide mixture added.	0·1*N*-$Na_2S_2O_3$ for back titration.	Bromine used up.	Calculated amount of bromine.
0·1 g.	0·1 g.	30 c.c.	8·3 c.c.	0·5096 g.	0·5106 g.
0·05	0·2	20	16·1	0·255	0·2553
0·05	0·15	20	16·1	0·255	0·2553
0·02	0·1	20	35·3	0·1016	0·1021
0·02	0·1	20	35·3	0·1016	0·1021

Agreement between the amount of bromine used up and that calculated on the basis that one mol. of phenol uses up 3 mols. of bromine, justifies the use of this method in the estimation.

Estimation of the Decomposition of Anisole after Treatment with Hydrochloric Acid.

0·5 G. of anisole with 6 c.c. of 10*N*-hydrochloric acid was heated in a sealed tube at 130° for 2 hours. The phenol liberated during the decomposition was then estimated as above and the results obtained are given below.

Expt.	Bromate-bromide mixture added.	0·1*N*-$Na_2S_2O_3$ required for back titration.	Phenol liberated.	Percentage decomposition of the ether.
I.	50 c.c.	30 c.c.	0·141 g.	32·4
II.	,,	31·5	0·1386	32
III.	,,	31	0·131	32
IV.	,,	30·5	0·1402	32·3
V.	,,	30	0·141	32·2
			Mean	32·22

Similar procedure was followed in the case of most ethers.

The following procedure was followed in the case of ethers where bromate-bromide mixture did not give satisfactory results.

Estimation of m-*Bromoanisole in a Mixture of* m-*Bromoanisole and* m-*Bromophenol.*

m-Bromoanisole is estimated by extracting it with ether from an alkaline solution. The ethereal solution is evaporated and then the ether directly estimated by weighing.

Weight of *m*-bromoanisole taken.	Weight of *m*-bromophenol added.	Weight of *m*-bromoanisole found.
0·5 g.	0·2 g.	0·496 g.
0·5	0·1	0·498
0·4	0·3	0·3975

Agreement between the values of *m*-bromoanisole estimated and that actually taken justifies the use of this method in the the estimation of *m*-bromoanisole, when treated with hydrochloric acid.

Estimation of the Decomposition of m-*Bromoanisole after Treatment with Hydrochloric Acid.*

A mixture of 0·5 g. of *m*-bromoanisole and 6 c.c. of 10*N*-hydrochloric acid was heated in a sealed tube at 130° for two hours. The phenol liberated during the decomposition was then estimated by the above method and the results obtained are given below.

Bromate-bromide mixture added.	0·1*N*-$Na_2S_2O_3$ required for back titration.	Phenol liberated.	Percentage decomposition of the ether.
0·5 c.c.	0·491 c.c.	0·010 g.	2·1
0·5	0·489	0·011	2·28
0·5	0·488	0·012	2·4
			Mean 2·28

Tabular Summary of Results.

Ether. (0·5 g. taken)	Percentage decomposition suffered at 130°. with 10*N*-HCl (6 c.c.).	with 5-HCl (6 c.c.).	Percentage decomposition at 100° with 10*N*-HCl (6 c.c.).
1. Anisole	33	—	—
2. Phenetole	14·8	—	—
3. *m*-Nitroanisole	6·4	1·3	1·29
4. *o*- „	10·88	1·95	1·9

Tabular Summary of Results—Contd.

Ether. (0·5 g. taken)	Percentage decomposition suffered at 130°		Percentage decomposition at 100°
	with 10*N*-HCl (6 c.c.).	with 5*N*-HCl (6 c.c.).	with 10*N*-HCl (6 c.c.).
5. *p*-Nitroanisole	12·77	2·4	2·3
6. *m*-Chloroanisole	3·55	—	—
7. *o*- ,,	9·9	—	—
8. *p*- ,,	12·8	—	—
9. *m*-Bromoanisole	2·23	—	—
10. *o*- ,,	4.67	—	—
11. *p*- ,,	6·8	—	—
12. *m*-Methylanisole	11·4	—	—
13. *o*- ,,	12·1	—	—
14. *p*- ,,	16·1	—	—
15. *m*-Aminoanisole	12·0	—	—
16. *o*- ,,	35.5	—	—
17. *p*- ,,	75·0	—	33·25
18. *m*-Acetylanisole	12·0		
19. *o*- ,,	58·8		
20. *p*- ,,	68·3	—	8 8
21. 2 : 4-Dinitro-anisole	5·4		
22. 3 : 5-Dinitro-anisole	3·3		
23. 2 : 4 : 6-Tribromo-ansiole	3·7		
24. *p*-Nitrophenetole	5·34		
25. *p*-Chlorophenetole	6.3		
26. *p*-Bromophenetole	3·5		
27. *p*-Methylphenetole	5·4		
28. Methyl ether of *α*-naphthol	15·7		
29. Methyl ether of *β*-naphthol	26·8		
30. Methyl ether of *ar.* tetrahydro-*α*-naphthol	9·2		

Discussion of Results.

(1) *m*-Derivatives decompose to the least and *p*-derivatives to the greatest extent, the corresponding *o*-compound having an intermediate value.

(2) Acidic atoms or groups like Br, Cl, NO_2 increase the stability of the ethers. Acetyl group, however, is an exception while methyl group behaves like an acidic radicle.

(3) Ethyl ethers decompose less readily than methyl ethers.

(4) Increase in the number of negative substituents increases the stability of the ethers.

(5) α-Naphthol methyl ether is less stable than its tetrahydro-derivative.

(6) Amino-group lessens the stability of the ethers.

CHEMICAL LABORATORY,
FERGUSSON COLLEGE, POONA.

Received June 26, 1931.

Chemical Examination of the Marking-nut (*Semecarpus Anacardium*, Linn).

By P. Parameswaren Pillay and Salimuzzaman Siddiqui.

Semecarpus anacardium, Linn (Hindi, *Bhilawan*, English, Marking-nut) grows in the tropical outer Himalayas and the hotter parts of India. Dymock ("Pharmacographia Indica", Vol. I. p. 389, and Kirtikar and Basu ("Indian Medicinal Plants", Vol. I. p. 384) may be referred to for the details of its history and uses. It may, however, be stated here that the black corrosive juice of the pericarp of the nut, which raises painful blisters on the skin but whose internal administration in dilution with emollient oils is considered safe in fairly large doses, has been found to be of great medicinal value, internally in cases of rheumatism, epilepsy, nervous debility, piles and dyspepsia, externally for eczema, lepra and several other diseases of the skin. It is also used by *dhobis* as an indelible marking ink in admixture with lime.

In spite of its enormous therapeutical significance, the chemical work done on the drug was limited to a conjecture ("Pharmacographia Indica," Vol. I. p. 392) that the tarry oil of its pericarp must be similar to that obtained from the pericarp of cashew nut (*Anacardium occidentale*), which consists of about 90 per cent. of an oxy-acid named anacardic acid, $C_{22}H_{32}O_3$ (Ruhemann and Skinner, *Ber.*, 1887, **20**, 1861; also *J. Chem. Soc.*, 1887, **51**, 663) and 10 per cent. of a higher, non-volatile alcohol called cardol, $C_{21}H_{30}O_2$ (Stadeler, *Annalen*, 1847, **63**, 137) and an investigation by Naidu (*J. Indian Inst. Sci.*, 1928, **8A**, 129), who claims to have isolated from it catechol and a monohydroxyphenol, $C_{18}H_{30}O$, which he called anacardol, besides two acids, and a fixed oil from the kernel of the nut.

As a result of our investigations we have succeeded in establishing that neither anacardic acid and cardol nor catechol and anacardol are present in Bhilawan, and have isolated the following products from the black juice of the pericarp, of which we obtained 28 to 36 per cent. on the weight of the nut as against 21 to 25 per cent. got by Naidu (*loc. cit.*).

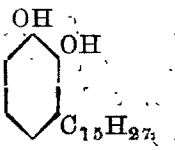
1. A monohydroxyphenol, which boils at 185-90°/2·5 mm. congeals below 25° to a fatty mass, forms 0·1 per cent. of the extract, and to which we have given the name "Semecarpol."

2. An *o*-dihydroxy-compound, $C_{21}H_{32}O_2$, which distils constantly at 225-26°/3 mm., congeals below 5°, and forms 46 per cent. of the juice (15 to 17 per cent. of the nut). We have called it "Bhilawanol."

3. A tarry corrosive residue, out of which no further chemical individual could be isolated even after repeated purification by means of solution in dilute alcohol and precipitation with alcoholic lead acetate.

Apart from the isolation and investigation of these products we also examined the alcoholic extract of the pericarp, after its exhaustion with ether and the ethereal extract of the kernel. The former was found to contain an ether-soluble and an ether-insoluble acid besides tannic acid, and the latter, 32·3 per cent. of a fatty oil; but as these products did not appear to be of any therapeutical interest they were not studied further.

Constitution of Bhilawanol.—From the analysis of bhilawanol and the determination of its molecular weight, bromine value, and hydroxyl groups we fixed on the molecular formula, $C_{21}H_{32}O_2$. That catechol formed the nucleus of bhilawanol was suggested by its colour reactions and supported by the isolation of catechol from the products of its dry distillation. The diacetyl, dibenzoyl, and dimethyl ether derivatives of bhilawanol were prepared and gave analytical results answering to the formula mentioned below, but none of them formed a solid. Of the other derivatives it was possible to get



only the naphthylurethane as a solid, melting at 138-40° which, however, could not be crystallised. On hydrogenation of bhilawanol with the help of platinum black (and crystallisation of the resulting product out of toluene), the hydro-derivative was obtained in quantitative yield as long colourless silky needles melting sharply at 57-58°. When oxidised with potassium permanganate in acetone solution hydrobhilawanol gave in good yield an acid, which was identified as palmitic acid. This proved bhilawanol to contain a single, normal, unsaturated C_{15}-side-chain, attached to a catechol nucleus. To fix

the position of this side-chain we oxidised diacetylbhilawanol with permanagnate in acetone solution, and succeeded in obtaining an acid which on hydrolysis gave the colour reactions of 1:2:3-catecholcarboxylic acid.

The melting point of hydrobhilawanol and the isolation of palmitic acid from its oxidation products suggested to us the possibility of its being identical with hydrourushiol ($C_{21}H_{36}O_2$), which was obtained by Majima and co-workers on hydrogenation of urushiol, the chief constituent of Japan lacquer, *Ki-urushi*, the dried juice of *Rhus vernicifera*, (*Ber.*, 1922, **55**, 172 and preceding papers). This view was further supported by our obtaining both a mono- and a dinitro-product from the dimethyl ether after Majima (*Ber.*, 1913, **46**, 4080) who found out that only 1:2:3- and not 1:2:4-catechol derivatives of this type yield a dinitro-product. We may note in this connection, however, that the nitric acid (*d* 1·52) recommended in the reference invariably gave only oily oxidation products and nitric acid (*d* 1·48) had to be used in order to get the crystalline dinitro-derivative.

The identity of hydrobhilawanol and hydrourushiol was finally established by the fact that the melting points of hydrobhilawanol and its dibenzoate and dimethyl ether derivatives, prepared by us, showed no depression when mixed with the corresponding derivatives of hydrourushiol, very kindly sent to us by Dr. Riko Majima of Japan.

Majima and co-workers (*loc. cit.*) have conclusively shown after an exhaustive examination of urushiol that it is a mixture of compounds; which differ from one another only in the number and position of the double bonds contained in the normal carbon side-chain, and which it is not possible to separate with the help of chemical methods at our command at present, but that in so far as this mixture gives a single chemical individual, hydrourushiol, on reduction, it is quite legitimate to keep to the name urushiol for this mixture as well as the general molecular formula $C_{21}H_{32}O_2$, for convenience of reference. In consideration of these findings and taking into account the difference in the physical characteristics of urushiol (b.p. 200-10°/5 mm.; $d_4^{21\cdot5}=0\cdot9687$; $n_D^{30}=1\cdot5234$) and bhilawanol (b. p. 213-14°/1 mm.; $d_4^{30}=0\cdot9542$; $n_D^{30}=1\cdot5032$), particularly the strikingly constant boiling point of the latter, we hold that while hydrobhilawanol and hydrourushiol are fully identical chemical individuals, bhilawanol itself is of slightly

different and more uniform character than urushiol, which contains about 10 per cent. of hydrourushiol ($C_{21}H_{36}O_2$) along with the *o*-dihydroxy-compounds, answering to the general formulae, $C_{21}H_{34}O_2$, $C_{21}H_{32}O_2$ and probably also $C_{21}H_{30}O_2$ (*Ber.*, 1922, 55, 175), Indeed, it may be due to its greater uniformity that bhilawanol congealed below 5° to a fatty mass and that we easily obtained a solid naphthylurethane of bhilawanol, while urushiol failed to give any solid derivative.

Semecarpol.—The quantity of this phenol was so small that we could not undertake its detailed examination. It was, however, proved that it is distinct from bhilawanol, by means of reduction, whereby a crystalline hydrogenated product was obtained, which melted at 51-52°, and showed a large depression in its melting point when mixed with hydrobhilawanol. Its monophenolic character was established by determination of its hydroxyl content. Its analysis suggested the empirical formula, $C_{17}H_{28}O$, but as the product was too little to be sufficiently purified, the formula could not be definitely fixed upon.

From the tarry residue, left after distillation of bhilawanol, it was not possible to get any solid hydro-derivative on reduction. The elementary analysis of a purified fraction of it and determination of its molecular weight and hydroxyl content show that it is a mixture of high molecular resinous phenols having nearly the same empirical formula as bhilawanol. Subjected to destructive distillation it yielded a mixture of high-boiling phenols and hydrocarbons from which no catechol could be isolated, which would suggest the absence of catechol nucleus in the tarry products and form an argument against the tar being a mere polymer of bhilawanol, because the products of dry distillation of the latter contain catechol as the chief phenolic constituent. Majima got a similar corrosive residue after distillation of urushiol from *Ki-urushi* and suggested that it was the product of polymerisation of urushiol, but this does not appear probable because like bhilawanol, urushiol also is not observed by Majima to show any tendency towards polymerisation on subsequent distillation.

In reference to Naidu's (*loc. cit.*) investigations, we have to note that while we have found catechol to be absent as such in juice of the pericarp, it could be isolated from the products of decomposition of bhilawanol, and that from the account he has given of the isolation of what he describes as anacardol, we feel justified in suspecting that it was a product of decomposition. This

would explain his failure to get bhilawanol, which constitutes nearly half the ethereal extract, as well as his low yields, the difficulty he finds in freeing the high-boiling anacardol from catechol and his failure to get a proper acetyl derivative.

Apparently the most interesting feature of our investigation is the parallel established between the active constituents of *Semecarpus anacardium*, Linn and *Rhus vernicifera*, which belong to the same natural order (*Anacardiaceae*), but are put to totally different uses in their native countries, for, as is evident from the reference on *Ki-urushi*, it is not reputed for any medicinal properties in Japan. Apart from the scientific interest involved in our results, they may also extend the utility of each plant beyond its present dimensions and open up possibilities of establishing *bhilawan* as a valuable addition to the list of the natural products used in lacquer industry.

Experimental.

The material used for our investigations was obtained from the local bazaar. The crushed pericarp on extraction with ether yielded 28 to 36 per cent. of a dark brown oily extract having $d\,\frac{30}{30} = 0{\cdot}9603$.

Absence of Catechol in the Extract.—The extract (500 g.) was shaken four times with 200 c.c. each of water. The aqueous layer on very careful examination was found to contain no catechol but a trace of bhilawanol in suspension which gave a faint green coloration with ferric chloride.

Anacardic acid and cardol, the constituents of the juice of the cashew nut were tested for with freshly precipitated lead hydroxide according to the method of Ruhemann and Skinner (*Ber.*, 1887, **20**, 1861) and were found to be absent.

Distillation in high vacuum was found to be the best method for the separation of the constituents of the extract. As a result of repeated fractional distillation below 3 mm. the following products were obtained.

Fraction 1.—A light yellow liquid boiling at 185-90°/2·5 mm. which congeals to a white fatty mass below 25° and forms only 0·1 per cent. of the total extract.

Fraction 2.—A golden yellow, slightly viscous liquid, boiling at 225-26°/3 mm. which forms about 46 per cent. of the weight of extract or 15 per cent. of the weight of the entire nut.

Residue.—A tarry non-volatile, dark brown, corrosive residue which forms 54 per cent. of the extract and 18 per cent. of the entire nut.

Examination of the Different Products.

Fraction 1: *Semecarpol.*—This fraction gives a white precipitate on the addition of alcoholic lead acetate and unlike Fraction 2, a fairly permanent green coloration with alcoholic ferric chloride indicating an *ortho*-phenol. On hydrogenation in absolute alcoholic solution in presence of platinum black according to the method of Willstätter (*Ber.*, 1908, **41**, 1475) a white solid was obtained, which when crystallised from ethyl acetate melted at 51-52° and showed a large depression of m.p. when mixed with hydrobhilawanol. (Found: C, 81·5; H, 11·3. $C_{17}H_{28}O$ requires C, 82·2; H, 11·3 per cent.). Estimated according to the method of Hibbert and Sudborough (*J. Chem. Soc.*, 1904, **85**, 933), it gave a hydroxyl content of 7·4% (one hydroxyl requires 6·9%). 0·234 G. of the substance titrated against bromine in dry chloroform solution in a freezing mixture took up 0·162 g. of bromine (calc. for 1 double bond, 0·151 g.).

Fraction 2: *Bhilawanol.*—This fraction, has the following physical constants: B. p. 225-26°/3 mm.; 213°-14°/1 mm.; $d_{30}^{30}=0·9591$ $n_D^{30}=1·5082$; $\alpha_D^{30}=$nil.

It congeals to a white fatty mass below 5°; with alcoholic ferric chloride it gives an evanescent green coloration, turning immediately to a black precipitate, and a violet-red coloration on further addition of a drop of alcoholic potash, indicating an *o*-dihydroxy-compound. With alcoholic lead acetate it gives a white precipitate which dissolves in ether with a green coloration. With caustic soda it gives a green phenolate insoluble in water but soluble in alcohol and ether, which darkens quickly on exposure to air due to oxidation. [Found: C, 79·8, 79·7; H, 10·7, 10·75. M. W. (cryoscopic in benzene), 345·3, 339·1. $C_{21}H_{32}O_2$ requires C, 79·8; H, 10·1 per cent. M. W., 316]. The hydroxyl content determined according to the method of Hibbert and Sudborough (*loc. cit.*) gave OH, 10·17, 10·24 (calc. for 2 OH, 10·7 per cent.).

Bromine-addition Product.—Bhilawanol (1·2 g.) titrated in dry cooled chloroform solution against bromine took up 1·16 g. (calc. for 2 double bonds, 1·21 g. bromine). Owing to the brownish-red

colour of the product the titration was followed by means of potassium iodide-st arch paper. The product, obtained on evaporation as a brown syrup, co uld neither be distilled nor obtained as a solid.

Bhilawanol diacetate was prepared by boiling bhilawanol (12 g.) with acetic anhydride (16 g.) in presence of anhydrous sodium acetate and was obtained as a yellow liquid (10·5 g.) b. p. 230°/2 mm.; $d_{30}^{30}=0·9822$; $n_D^{30}=1·4822$. It has a characteristic smell and does not react with lead acetate or ferric chloride, showing the absence of hydroxyl gro ups. (Found: C, 74·8; H, 9·3. $C_{25}H_{36}O_4$ requires C, 75·0; H, 9·0 per cent.).

Bhilawanol dimethyl ether was prepared by treatment of bhilawanol with methyl iodide and sodium ethylate in absolute alcohol in a hydrogen atmosphere and was obtained as a mobile light yellow liquid, b. p. 218°/3 5 mm.; $d_{30}^{30}=0·9325$; $n_D^{30}=1·4896$. (Found: C, 80·1; H, 10·8. $C_{23}H_{36}O_2$ requires C, 80·2; H, 10·4 per cent.).

Bhilawanol dinaphthylurethane was obtained by treating bhilawanol (1·1 g.) with naphthyl *iso*cyanate (1·13 g.) and dissolving the solid reaction product in hot alcohol from which it came down on cooling as a white powder melting at 138-40° (yield, 1·7 g.). (Found: N, 4·7. $C_{43}H_{46}O_4N_2$ requires N, 4·8 per cent.).

Distillation of Bhilawanol at Ordinary Pressure.

Bhilawanol (22 g.) subjected to dry distillation yielded 12·5 g. of total distillate, about 1 g. of which was found to be water. The remainder was separated by shaking in a hydrogen atmosphere with caustic soda solution into (*a*) phenols (3·5 g.) and (*b*) non-phenols (7·5 g.).

(*a*) *Phenols* obtained by the acidification of the caustic soda solution were fractionated. The first fraction boiling between 230° and 260° (1·3 g.) solidified. On crystalisation from benzene it gave crystals (0·7 g.) melting at 104° and identified as catechol by mixed melting point method. (Found: C, 65·05; H, 5·42. $C_6H_6O_2$ requires C, 65·42; H, 5·4 per cent.).

(*b*) *Non-phenols* were fractionated and the chief fraction boiling at 245-48° (1·8 g.) analysed, the results indicating a hydrocarbon. (Found: C, 85·38; H, 13·48 per cent.).

Oxidation of Bhilawanol Diacetate.—The substance (3·2 g.) was dissolved in a mixture of acetone (100 c.c.) and water (30 c.c.) and

acetic acid (6 c.c.) and then powdered potassium permanganate (8 g.) in small quantites at a time was added to the solution. Worked up in the usual manner, it yielded 2·1 g. of acids, which were hydrolysed with alcoholic potash in a hydrogen atmosphere. The resulting acids (1·7 g.) were not obtained solid, but gave the colour reactions of *o*-catechuic acid. A large-scale oxidation was not conducted as it was rendered unessential by our identifying hydrobhilawanol with hydrourushiol.

Catalytic Reduction of Bhilawanol.—To a solution of bhilawanol (3·5 g.) in absolute alcohol (6 c.c.) was added 1 g. of platinum black prepared according to the method of Willstätter and Mayer (*Ber.*, 1903, **41**, 1475, 2199) and the mixture was placed in a closed bottle attached to a hydrogen generator and shaken in a shaking machine. The absorption of hydrogen ceased in five hours. The resulting product, when filtered from the platinum black and freed of the solvent on the water-bath, gave the hydro-product as a crystalline solid. On recrystallisation from toluene hydrobhilawanol was obtained as white needles (3·2 g.) melting at 57 58°. (Found : C, 78·43 ; H, 11·60. $C_{21}H_{36}O_2$ requires C, 78·62 ; H, 11·32 per cent.).

Oxidation of Hydrobhilawanol: Palmitic Acid.—To hydrobhilawanol (2·2 g.) disolved in acetone (200 c.c.) and water (30 c.c.) was added a solution of potassium permanganate (7 g.) in acetone (200 c.c.) and water (30 c.c.). The mixture was warmed until decolourised and filtered. From the filtrate acetone was removed on a water-bath and the aqueous residue acidified with hydrochloric acid. The acid thereby liberated (1·05 g.) after two crystallisations out of 95% alcohol melted at 59-60°, the melting point showing no depression on admixture with a sample of pure palmitic acid.

Diacetyl Hydrobhilawanol.—It was prepared by acetylation of hydrobhilawanol with acetic anhydride and anyhydrous sodium acetate and was obtained as shining white plates, from alcohol, m.p. 51°.

Dibenzoyl hydrobhilawanol was prepared by treating hydrobhilawanol (0·5 g.) in dry ether (5 c.c) with benzoyl chloride (1 g.) and working up the reaction product in the usual manner. On crystallisation out of alcohol the dibenzoate melted at 59-60°.

The *dimethyl ether* prepared by the reduction of bhilawanol dimethyl ether (2 g.) in ethereal solution in presence of platinum black, melted at 36-37°, when crystallised out of alcohol (1·8 g.).

The melting points of hydrobhilawanol and its two last mentioned derivatives showed no depression on admixture with the corresponding derivatives of urushiol.

Mononitrohydrobhilawanol Methyl Ether.—Hydrobhilawanol dimethyl ether (0·8 g.) in glacial acetic acid (3 c.c.) was treated with a mixture of nitric acid (*d* 1·48, 3 c.c) and glacial acetic acid (5 c.c.). The mixture was warmed for half a minute on the water-bath and then kept aside to cool. The resulting yellow crystals when crystallised from alcohol gave 0·4 g. of light yellow needles, m.p. 71-72°.

Dinitrohydrobhilawanol Dimethyl Ether.—The mononitro-derivative (0·5 g.) was treated with nitric acid (*d* 1·48, 1 c.c.), warmed for 2 minutes on the water-bath until it dissolved and then quickly cooled and diluted. The dinitro-derivative, which separated out as a solid, crystallised out of alcohol in light yellow needles melting at 83°.

The Tarry Residue.—This forms more than 50% of the ether extract and was obtained after the distillation of bhilawanol as a very viscous dark mass. It was purified by dissolving in 80% cold alcohol, which leaves a thick dark resinous mass undissolved, trea ting the alcoholic solution with lead acetate and liberating the tarry phenolic product from the lead salt with hydrochloric acid. It dissolves in alcoholic potash with a fairly permanent grass-green coloration. With ferric chloride it gives a very transient green colour followed by a black precipitate. With lead acetate it forms a green precipitate. It was found that it could be acetylated and etherified just like bhilawanol, but none of the products could be distilled or made to solidify even when hydrogenated. On distillation at ordinary pressure the tar (20 g.) gave a mixture of phenols (2·7 g.) and non-phenols (3 g.) but no catechol was obtained from the distillate. The M. W. found by the depression of the freezing point of benzene was nearly 1000. Its reactions indicate that it is a mixture of high molecular resinous phenols but it could not be further investigated owing to the impossibility of purifying it or its derivatives. (Found: C, 78·74; H, 10·09. $(C_{21}H_{32}O_2)_n$ requires C, 79·8 ; H, 10·1 per cent.).

In conclusion we heartily thank Dr. Riko Majima of Japan for kindly providing us with samples of hydrourushiol and two of its derivatives.

RESEARCH INSTITUTE,
A. V. & U. TIBBI COLLEGE, DELHI.

Received July 16, 1930.

Coumaryl 6-*iso*Thiocyanate.

By Biman Bihari Dey and Tiruvenkata Rajendra Seshadri.

6:6′-Dicoumarylthiocarbamide is formed on boiling an alcoholic solution of 6-aminocoumarin with carbon disulphide. The reaction is ordinarily very slow, but is accelerated as usual by the addition of small amounts of sulphur. The use of sodium hydroxide which is generally employed for such condensations is inadvisable in this case, as it causes decomposition of the thiocarbamide. The latter is remarkably stable, however, in presence of acids, and may be boiled with concentrated hydrochloric acid without undergoing any change.

Thiophosgene has been found to be a suitable reagent to employ for the preparation of the *iso*thiocyanate from the aminocoumarin. Dyson and George (*J. Chem. Soc.*, 1925, **125**, 1702) state that the reaction between aniline and thiophosgene proceeds in the following manner,

$$C_6H_5NH_2 + CSCl_2 \longrightarrow [C_6H_5NH_2Cl\cdot CSCl] \longrightarrow C_6H_5NH\cdot CSCl \longrightarrow C_6H_5\cdot NCS$$

the intermediate phenylthiocarbamyl chloride, $C_6H_5\cdot NH\cdot CS\cdot Cl$, being actually isolated by them. The interaction of aminocoumarin and thiophosgene in dry benzene solution gave a product which could not be obtained pure but which probably corresponded to the thiocarbamyl chloride as it readily decomposed in contact with water into aminocoumarin hydrochloride and coumarylthiocarbimide. A better and purer yield of the thiocarbimide was obtained by carrying out the reaction in aqueous medium (*cf.* Dyson and George, *loc. cit.*), the amount of thiocarbonyl chloride used being slightly in excess of that required according to the following equation:—

$$3\ C_9H_5O_2\cdot NH_2 + CSCl_2 = C_9H_5O_2\cdot NCS + 2\ C_9H_5O_2\cdot NH_3Cl$$

The objectionable nature of thiophosgene made it desirable to search for a process in which the use of this reagent could be dispensed with altogether, and it was found that the method worked out

by Werner (*J. Chem. Soc.*, 1891, **59**, 396) could be applied with success to the present case. When dicoumarylthiocarbamide is boiled with acetic anhydride, a vigorous reaction ensues and the carbamide is converted almost quantitatively into a mixture of acetylaminocoumarin and coumaryl *iso*thiocyanate, thus:

$$CS(NH\cdot C_9H_5O_2)_2 + (CH_3CO)_2O = CH_3\cdot CO\cdot NH\cdot C_9H_5O_2 + C_9H_5O_2\cdot NCS + CH_3\cdot CO_2H$$

The thiocarbimide is readily separated from the acetylaminocoumarin which is much more soluble in acetic acid. The reactions of this thiocarbimide with a few amino-and hydroxy compounds are also described.

Experimental.

6: 6′-*Dicoumarylthiocarbamide.*—6-Aminocoumarin (2 g.) was boiled for 6 hours with alcohol (30 c.c.), carbon disulphide (10 c.c.) and sulphur (0·5 g.). The clear solution slowly deposited a bulky amorphous solid which was filtered and washed, first with carbon disulphide and then with dilute hydrochloric acid. It was very sparingly soluble in the common organic solvents but could be crystallised from boiling nitrobenzene as colourless rhombic prisms, m.p. 250-52° (yield 2 g.). (Found: N, 7·8; S, 8·5. $C_{19}H_{12}O_4N_2S$ requires N, 7·7; S, 8·8 per cent.).

The substance readily dissolved in alkali hydroxides to form yellow solutions from which it could be reprecipitated by acidifying; it remained unchanged on boiling with concentrated hydrochloric acid or on treating with concentrated sulphuric acid at 100° or even on boiling with acetyl chloride for half an hour. It was decomposed on continued boiling with caustic potash.

Coumaryl-6-thiocarbimide: (1) *From dicoumarylthiocarbamide.*—Dicoumarylthiocarbamide (2 g.) was boiled with acetic anhydride (10 c.c.) over a sand-bath for about 5 minutes. The resulting clear solution, on cooling, was filled with a thick mass of colourless needles. Water was then added and the mixture boiled to decompose all acetic anhydride, and filtered hot. The residue, which was almost pure, was further boiled twice with small quantities of dilute acetic acid and filtered.

The product crystallised from benzene as colourless needles, m.p. 186-87° (yield 70 p. c.). (Found: N, 7·1; S, 15·9. $C_{10}H_5O_2NS$ requires N, 6·9; S, 15·7 per cent.),

The combined acetic acid filtrate deposited, on cooling, a bulky crystalline precipitate and a further quantity was produced on neutralising the solution with ammonia. It crystallised from boiling water as colourless flat needles melting at 220-21° and was found to be identical with 6-acetylaminocoumarin.

(2) *From 6-Aminocoumarin and Thiocarbonyl Chloride.*—Thiocarbonyl chloride in aqueous suspension was treated with a little less than three molecular quantities of 6-aminocoumarin which was added in small quantities at a time, the reaction mixture being warmed up to 60° and stirred mechanically. The bulky amorphous precipitate was filtered, washed with dilute hydrochloric acid, dried on a porous plate and twice crystallised from boiling benzene, using animal charcoal, when 6-coumarylthiocarbimide was obtained as colourless needles, m.p. 186-87°. It was identical with the product obtained from the dicoumarylthiocarbamide mentioned above.

It is insoluble in water, dilute mineral acids or dilute alkali solutions and it is only slowly decomposed by glacial acetic acid to produce acetylaminocoumarin. When a boiling alcoholic solution of the substance is mixed with a similar solution of 6-aminocoumarin a bulky precipitate of 6:6′-dicoumarylthiocarbamide is obtained.

Monocoumaryl-6-thiocarbamide was slowly deposited as heavy colourless crystals when a boiling alcoholic solution of the thiocarbimide was treated with an excess of concentrated aqueous ammonia. It could be easily crystallised from alcohol, m.p. 234-35° (decomp.). (Found: N, 12·9. $C_{10}H_8O_2NS$ requires N, 12·7 per cent.).

Phenyl-6-coumarylthiocarbamide was obtained in two ways, *viz.*, by boiling for about two hours a solution in alcohol or benzene of equimolecular quantities of (1) 6-coumarylthiocarbimide and aniline and (2) phenylthiocarbimide and 6-aminocoumarin. The product was filtered, washed thoroughly with dilute hydrochloric acid and after drying on a porous plate, crystallised from benzene. It came down as colourless rectangular prisms, m.p. 169-70° (decomp.). (Found: N, 9·6. $C_{16}H_{12}O_2N_2S$ requires N, 9·5 per cent.).

When the product obtained by its decomposition at the melting point was repeatedly crystallised from nitrobenzene, it melted at 252°, and was found to be identical with 6:6′-dicoumarylthiocarbamide.

Phenyl-6-coumarylthiosemicarbazide was produced in a crystalline condition by boiling equimolecular quantities of coumarylthiocarbimide and phenylhydrazine in benzene solution for an hour. After

cooling and filtering, it was washed with small quantities of hot benzene and later, with dilute hydrochloric acid. It then crystallised from boiling benzene as colourless needles, m.p. 171-72°. (Found: N, 13·4. $C_{16}H_{13}O_2N_3S$ requires N, 13·5 per cent.).

Ethyl coumaryl-6-thiocarbamate was obtained as thin plates when an alcoholic solution of coumaryl-6-thiocarbimide was boiled under reflux for 5 hours and then cooled. After recrystallisation from alcohol it melted at 167-68°. (Found: N, 5·4. $C_{13}H_{11}O_3NS$ requires N, 5·6 per cent.).

6-*Thio*-p-*tolylaminocoumarin* was prepared by adding anhydrous aluminium chloride to a solution of coumaryl-6-thiocarbimide in dry toluene and heating it on the water-bath for 2 hours. On pouring the product into water a flocculent precipitate was obtained which crystallised from alcohol as pale yellow needles, m.p. 253-54°. (Found: N, 4·9. $C_{17}H_{13}O_2NS$ requires N, 4·7 per cent.).

6:6′-*Di*-4:7-*dimethylcoumarylthiocarbamide* was obtained in good yield from 6-amino-4:7-dimethylcoumarin and carbon disulphide. It crystallised from nitrobenzene as colourless prisms, m.p. 258-60°. (Found: N, 6·8. $C_{23}H_{20}O_4N_2S$ requires N, 6·7 per cent.).

4:7-*Dimethylcoumaryl-6-thiocarbimide* was prepared by the same two methods as have been described in the case of coumaryl-6-thiocarbimide. It crystallised from boiling benzene as colourless needles, m.p. 235°. (Found: N, 6·2. $C_{12}H_9O_2NS$ requires N, 6·1 per cent.).

In boiling alcoholic solution it combines with 6-amino-4:7-dimethylcoumarin to produce 6:6′-di-4:7-dimethylcoumarylthiocarbamide; with concentrated ammonia it yielded *mono*-4:7-*dimethylcoumarylthiocarbamide* as large prisms, m.p. 241° (decomp.), and with aniline it formed 4:7-*dimethylcoumarylphenylthiocarbamide* crystallising in rectangular prisms, m.p. 192° (decomp.).

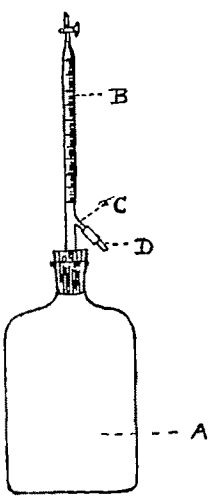
PRESIDENCY COLLEGE,
MADRAS.

Received July 3, 1931.

A Simple Apparatus for Elementary Classes for Determining Partial Pressures of Gases from their Aqueous Solutions by a Static Method.

By U. Mudlagiry Nayak and S. Lakhminarayanan.

The bottle (A) is fitted with an inverted burette (B), having an inclined side-tube (C), which may be closed by a rubber tube and glass plug (D). After the capacity of the apparatus has been determined, a known volume of a solution of sulphur dioxide of known strength (determined by standard iodine and thiosulphate) is introduced through (C), which is then closed. The bottle is shaken several times and after about 20 minutes, while (A) is in an inverted position, a known volume of the solutions is withdrawn and titrated. From the laboratory temperature and the concentrations of the original and residual sulphur dioxide solution, the weight of sulphur dioxide in the gaseous phase is obtained and the partial pressure of sulphur dioxide calculated. The results given below show the accuracy. For two solutions containing 1·782 g. and 1·923 g. of SO_2 respectively per 1000 g. of water, the partial pressures 10·53 and 12·63 mm. of Hg were obtained. The values given by Sherwood (*Ind. Eng. Chem.*, 1925, **17**, 745) are respectively 10·4 and 11·9 mm.



Chemical Laboratory,
Presidency College, Madras.

Received June 1, 1931.

A Preliminary Note on the Catalytic Oxidation of Paraffins.

By M. Goswami and S. K. Chatterjee.

Air was passed through paraffin (m. p. 49°, iodine value 1·5 and of approximate composition $C_{24}H_{50}$) kept just below the boiling point and the mixed vapour was conducted over nickel prepared by reducing nickel oxide by means of hydrogen at 200°; the rate of air was 0·01 cubic feet per minute. The issuing vapour was condensed in several successive receivers and the liquid thus obtained, was slightly acidic and gave all the tests of aldehydes. This was freed from the unchanged paraffin, by means of methyl alcohol, in which paraffin is not soluble. The methyl alcohol was evaporated away and the remaining liquid was treated with sodium bisulphite. Aldehyde was then set free from the bisulphite compound, taken up with ether, the ethereal solution dried and the ether evaporated off. The residue was then fractionally distilled at 15—17 mm. The following fractions were obtained:

		Temperature.	Yield per 100 g. of paraffin used.
I.	Up to	70°	1·25 g.
II.	,,	70°—105°	3·30
III.	,,	105°—115°	3·30
IV.	,,	115°—130°	6·60
V.	,,	130°—150°	5·30

Boiling points of the saturated aldehydes C_8-, C_9-, C_{10}- and C_{11}- are respectively 72° (20 mm.), 81° (14 mm.), 91° (11 mm), and 116° (18 mm.).

It thus appears that the liquid obtained by the oxidation of paraffins ($C_{24}H_{50}$) under the conditions of the experiment consists of the higher aldehydes. The total conversion of the paraffins into aldehydes was about 20%. Further investigations are in progress.

University College of Science and Technology,
Calcutta.

Received May 7, 1931.

A Note on the Volumetric Estimation of Hydrogen Peroxide in Presence of Potassium Persulphate.

By U. Mudlagiry Nayak.

Friend (*J. Chem. Soc.*, 1904, 85, 597, 1533; *ibid.*, 1905, 87, 1867) has shown that in ordinary circumstances an accurate estimation of hydrogen peroxide in presence of potassium persulphate by direct titration with potassium permanganate is not possible, because during titration H_2O_2 and $K_2S_2O_8$ react with each other in the sense of the equation, $H_2O_2+K_2S_2O_8=K_2SO_4+H_2SO_4+O_2$. Fairly satisfactory results may be obtained by correcting for the H_2O_2 consumed as above during titration.

The total available oxygen in one portion of the mixture is first estimated by the $FeSO_4-KMnO_4$ method (1). The same volume of the solution is then titrated with $KMnO_4$ and the volume of $KMnO_4$ required is noted (2). The amount of persulphate left behind in the liquid from (2) is finally determined by the $FeSO_4-KMnO_4$ method (3).

If the total available oxygen in (1) $\equiv x$ c.c. of standard K Mn O_4,
the permanganate required in (2) $\equiv y$ c.c. ,, ,,
and the residual persulphate in (3) $\equiv z$ c.c. ,, ,,
then the quantity of H_2O_2 which interacted with $K_2S_2O_8$ during titration $\equiv \frac{(x-y-z)}{2}$ c.c.

Hence the amount of H_2O_2 in the solution taken for analysis $\equiv y+\frac{(x-y-z)}{2}$ c.c.

Example.—20 C.c of a solution of H_2O_2 required 17·55 c.c. of 0·1*N*-$KMnO_4$. 20 C.c. of the same H_2O_2 were mixed with 20 c.c. of a solution of $K_2S_2O_8$ and the total available oxygen in the mixture was found to be equal to 34·16 c.c. of $KMnO_4$ (x). Another 20 c.c. of H_2O_2 were mixed with 20 c.c. of $K_2S_2O_8$ and the mixture titrated with $KMnO_4$ in the usal way. 16·90 C.c. of $KMnO_4$ (y) were

required. The amount of $K_2S_2O_8$ in the titrated liquid was then determined and was equivalent to 15·89 c.c. of $KMnO_4$ (z).

The amount of H_2O_2 in the mixture $= 16{\cdot}9 + \frac{(34{\cdot}16 - 16{\cdot}9 - 15{\cdot}89}{2}$ c.c. $= 17{\cdot}59$ c.c. of 0·1 N-$KMnO_4$. Theoretical value $= 17{\cdot}55$ c.c.

The results of a few more experiments carried out in the same manner are given in the following table.

Column I gives the weight of $K_2S_2O_8$ in grams in the mixed solution. Column II gives the total available oxygen in the solution in terms of 0·1 N-$KMnO_4$ (x). Column III gives the volume of 0·1 N-$KMnO_4$ required for titrating the H_2O_2 in mixture (y). Column IV gives the residual $K_2S_2O_8$ in the solution after titration with $KMnO_4$, in terms of 0·1 N-$KMnO_4$ (z). Column V gives the value of $y + \frac{(x-y-z)}{2}$. Column VI gives the theoretical value of H_2O_2 in mixture in terms of 0·1 N-$KMnO_4$.

I	II	III	IV	V	VI
$K_2S_2O_8$	x	y	z	$y + \frac{(x-y-z)}{2}$	
0·2136	32·50 c.c.	16·00 c.c.	15·10 c.c.	16·70 c.c.	16·70 c.c.
0·4272	48·80	15·46	30·45	16·66	16·70
0·6408	64·10	15·00	45·80	16·65	16·70
0·6408	64·10	14·90	45·70	16·65	16·70
0·2475	36·85	17·90	17·70	18·53	18·56
0·4950	50·46	12·82	35·60	18·84	18·86

The agreement between the values in columns V and VI is very satisfactory.

A similar method may be employed for estimating hydrogen peroxide in presence of permonosulphuric acid.

My thanks are due to Professor B. B. Dey for his kind and helpful criticism.

PRESIDENCY COLLEGE,
MADRAS.

Received July 7, 1931.

Attempts to Prepare Dyes from Fluorenone.

By Anukul Chandra Sircar and Khitish Chandra Bhattacharyya.

Since it is well known that in presence of a chromophoric group, a compact ring structure acts as an additional chromophore, it was thought of exploring the possibility of preparing dyes from fluorenone by taking it as a chromophoric seat and packing other groups round it. With this object in view the present investigation was undertaken. It may be mentioned here that hitherto no dyestuff had been prepared from fluorenone except those described by Underwood and Kochmann (*J. Amer. Chem. Soc.*, 1923, **45**, 3075).

The $-N=CH-$ group, like the azo-linking $-N=N-$ is known to enhance tinctorial properties (*cf.* Green and Sen, *J. Chem. Soc.*, 1910, **97**, 2242; Morgan and Reeves, *J. Chem. Soc.*, 1922, **121**, 1; Sircar and Sen-Gupta, *J. Indian Chem. Soc.*, 1924, **1**, 321) and successful attempts have been made of creating the azo-methine groups in the fluorenone molecule by condensing various aromatic aldehydes, *e.g.*, benzaldehyde, salicylaldehyde, *m* hydroxybenzaldehyde, *p*-hydroxybenzaldehyde, *m*-nitrobenzaldehyde, *o*-nitrobenzaldehyde, *p*-nitrobenzaldehyde, *p*-acetylaminobenzaldehyde, *p*-dimethylaminobenzaldehyde, resorcylaldehyde and vanillin with 2-aminofluorenone, the object being to investigate the effect of azo-methine groups on the colour of the compound.

Fluorenonephenylazo-methines are easily obtained and many of them are fairly deep coloured and form well-defined crystals, but are not satisfactory so far as their dyeing properties are concerned. They possess no affinity for cotton and are decomposed into the original components when boiled for some time with water in presence of an acid. Wool can however be dyed with them from one per cent. acetic acid bath between 80 and 85°. But though the bath is exhausted, even in that case the shades obtained on wool are neither very bright nor very deep. In their properties therefore the fluorenonephenylazo-methines closely resemble the phenanthraquinonephenylazo-methines described by Sircar and Sen-Gupta (*loc. cit.*).

A number of azo-derivatives have also been prepared by coupling 2-diazofluorenone chloride with various phenols and amines *e.g.* β-naphthol, dimethylaniline, phenol, salicylic acid, 2-hydroxy-3-naphthoic acid, naphthionic acid, 1-naphthol-4-sulphonic acid, diethyl-

aniline, R-acid (β-naphthol-3:6-disulphonic acid) and G-acid (β-naphthol-6:8-disulphonic acid.

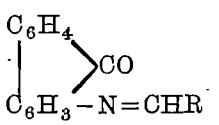
The fluorenoneazo-derivatives are obtained mostly in well-defined crystalline form and majority of them are deep coloured and possess well-developed dyeing properties. They dye wool evenly from one per cent. sulphuric acid bath in shades ranging from orange yellow to deep scarlet and bluish-violet.

Lastly, an attempt was made to prepare vat dyes from 2-aminofluorenone by condensing it with various dibasic acid chlorides, *e.g.*, oxalylchloride, phthalylchloride, carbonyl chloride, thionyl chloride, malonic acid (in presence of phosphorus pentachloride), succinic acid (in presence of phosphorus pentachloride) and glutaric acid (in presence of phosphorus pentachloride), but contrary to the expectation, the resulting fluorenonylamides could not be made to yield soluble vats with hydrosulphite. They however dye wool, though slowly, from an one per cent. sulphuric acid bath. But the shades obtained, though even, are invariably very light and rather disappointing.

Attempts to apply Ullmann's reaction to 2-bromofluorenone (Schmidt and Bauer, *Ber.*, 1905, **38**, 764) with a view to prepare anilinofluorenones were unsuccessful in the sense that simultaneously with the bromine atom the ketonic group was also attacked. The resulting products, being therefore of no interest, were not furthur investigated.

Experimental.

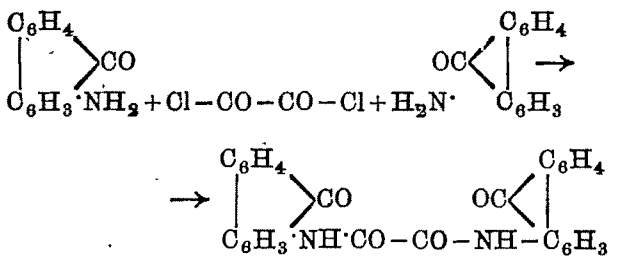
For the preparation of the azo-methines (described in Table A), equimolecular proportions of 2-aminofluorenone and the aldehyde are dissolved in the least quantity of alcohol, except where otherwise mentioned, and the solution heated on the water-bath until the separation of the solid is complete (the time required for the same has been noted in each case). The product is purified by crystallisation. The yield is generally almost theoretical. They are moderately soluble in alcohol, sparingly soluble in acetone or chloroform and insoluble in water and have the following general formula:



R=phenyl or substituted phenyl nucleus.

For the preparation of the fluorenoneazo-derivatives described in Table B, 2-aminofluorenone is diazotised (Diels, *Ber.*, 1901, **34**, 1764) and the 2-diazo-fluorenone chloride is coupled with the calculated quantity of the second component in the usual way.

Attempts to prepare Vat Dyes.—The condensation of the dibasic acid chlorides with 2-aminofluorenone is easily effected by heating for about two hours a solution of two molecules of the amino-quinone with somewhat more than one molecule of the acid chloride in nitrobenzene. The reaction takes place in the following way:



The condensation products are precipitated from the nitrobenzene solution on the addition of ether and are purified by repeatedly washing with ether and finally with water. They resist all attempts towards crystallisation, being insoluble in all organic solvents, and are reddish-brown or brownish-red amorphous bodies, not melting below 290°. They cannot be reduced to soluble vats. The compounds obtained are detailed in Table C.

TABLE A.

Fluorenone-2-azo-methine Derivatives.

	Name.	Method of preparation. A = 2-aminofluorenone.	Appearance and m.p.	Shade of dyeing on wool.	Analysis (nitrogen) Found.	Calc.
1.	Fluorenone-2-(1′-azo-methine benzene).	A + benzaldehyde (no solvent taken); heating for 3 hours.	Brown needles (from dilute alcohol); not melting below 290°.	Light pink-buff.	5·19	4·94 p.c.
2.	Fluorenone-2-(1′-azo-methine-2′-hydroxybenzene).	A + salicylaldehyde (standing overnight at ordinary temperature).	Orange-yellow needles (from hot alcohol); m.p. 230°.	Pinkish-orange.	4·9	4·68 ,,
3.	Fluorenone-2-(1′-azo-methine-3′-hydroxybenzene).	A + *m*-hydroxybenzaldehyde; heating for about 10 hours.	Brown needles (from hot alcohol); not melting below 290°.	Pinkish-buff.	49·6	4·68 ,,
4.	Fluorenone-2-(1′-azo-methine-4′-hydroxybenzene).	A + *p*-hydroxybenzaldehyde; heating for 3½ hours.	Deep orange crystalline powder (from hot alcohol); not melting below 290°.	Reddish-orange.	4·92	4·68 ,,
5.	Fluorenone-2-(1′-azo-methine-2′-nitrobenzene).	A + *o*-nitrobenzaldehyde; heating for 3 hours.	Deep yellow needles (from hot alcohol); m.p. 152°.	Yellow.	8·91	8·58 ,,
6.	Fluorenone-2-(1′-azo-methine-4′-nitrobenzene).	A + *p*-nitrobenzaldehyde; heating for 3 hours.	Orange-red crystalline powder (from hot alcohol); not melting below 290°.	Light yellowish-orange.	8·6	8·58 ,,
7.	Fluorenone-2-(1′-azo-methine-3′-nitrobenzene).	A + *m*-nitrobenzaldehyde; heating for 3 hours.	Orange needles (from hot alcohol); m.p. 213°.	Light orange-yellow.	8·9	8·58 ,,
8.	Fluorenone-2-(1′-azo-methine-4′-acetylaminobenzene).	A + *p*-acetylaminobenzaldehyde; heating for 9 hours.	Deep red needles (from hot alcohol); not melting below 290°.	Light pink.	8·39	8·28 ,,
9.	Fluorenone-2-(1′-azo-methine-4′-dimethylaminobenzene).	A + *p*-dimethylaminobenzaldehyde; heating for 4½ hours.	Deep red crystalline powder (from alcohol); m.p. 256°.	Brownish-yellow.	8·81	8·58 ,,
10.	Fluorenone-2-(1′-azo-methine-2′ : 4′-dihydroxybenzene).	A + resorcylaldehyde; heating for 4 hours.	Deep scarlet needles (from alcohol); not melting below 290°.	Reddish-orange.	4·61	4·44 ,,
11.	Fluorenone-2-(1′-azo-methine-3′-methoxy-4′-hydroxybenzene).	A + vanillin; heating for 3 hours.	Beautiful scarlet needles (from alcohol); not melting below 290°.	Light pinkish-violet.	4·44	4·25 ,,

TABLE B.

Fluorenoneazo-derivatives.

	Name.	Method of preparation. D=2-diazofluorenone chloride.	Appearance and m.p.	Solubilities.	Shade of dyeing on wool.	Analysis (nitrogen) Found.	Calc.
1.	Fluorenone-2-(1′)-azo-2′-naphthol.	D + β-naphthol.	Reddish-violet crystalline powder; m.p. 192°-94°	Slightly soluble in hot alcohol, insoluble in acetone, chloroform or water.	Reddish-violet.	8·13	800 p.c.
2.	Fluorenone-2-(1′)-azo-4′-dimethylaminobenzene.	D + dimethyl aniline.	Brownish-red crystalline powder (from hot alcohol); m.p. 198°	Moderately soluble in hot alcohol, sparingly soluble in acetone or chloroform and insoluble in water.	Reddish-brown.	13·1	12·84 ,,
3.	Fluorenone-2-(1′)-azo-4′-hydroxybenzene.	D + phenol.	Orange-red powder, (from alcohol); m.p. 218°.	Sparingly soluble in hot benzene or acetone, moderately in alcohol, insoluble in water.	Orange-yellow.	9·56	9·33 ,,
4.	Fluorenone-2-(1′)-azo-4′-hydroxy-3′-benzoic acid.	D + salicylic acid.	Yellowish-orange rectangular crystals; m.p. 216°.	Sparingly soluble in hot alcohol, insoluble in acetone or water.	Yellowish-brown.	8·37	8·1 ,,
5.	Fluorenone-2-(1′)-azo-2′-hydroxy-3′-naphthoic acid.	D + 2-hydroxy-3-naphthoic acid.	Bluish violet rectangular crystals; m.p. above 310°.	Slightly soluble in hot alcohol, insoluble in acetone, chloroform or water.	Bluish-violet.	7·2	7·1 ,,

TABLE B—*contd.*

	Name.	Method of preparation. D=2-diazofluorenone chloride.	Appearance and m.p.	Solubilities.	Shade of dyeing on wool.	Analysis (nitrogen) Found.	Calc.
6	Fluorenone-2-(2′)-azo-1′-naphthylamine-4′-sulphonic acid.	D + naphthionic acid.	Deep reddish-brown rectangular crystals (hot alcohol); m.p. above 310°.	Moderately soluble in hot alcohol or acetone, slightly soluble in hot water.	Reddish-pink.	9·89	9·79 p.c.
7.	Fluorenone-2-(2′)-azo-1′-hydroxy-naphthalene-4′-sulphonic acid.	D + 1-naphthol-4-sulphonic acid.	Reddish-violet crystals, (hot alcohol); m.p. above 310°.	Slightly soluble in water, moderately in hot alcohol and hot benzene.	Deep scarlet.	6·82	6·51 ,,
8.	Fluorenone-2-(1′)-azo-4′-diethylaminobenzene.	D + diethylaniline.	Deep brown crystalline powder (hot alcohol); m.p. above 310°.	Soluble in hot alcohol, hot benzene or hot acetone, insoluble in water.	Yellowish-brown.	11·9	11·83 ,,
9.	Fluorenone-2-(1′)-azo-2′-naphthol-4′ : 6′-disulphonic acid.	D + R-acid (2-naphthol-3 : 6-disulphonic acid).	Brownish-red crystalline powder (hot alcohol); m.p. above 310°.	Moderately soluble in water, soluble in much alcohol.	Brownish-red.	5·75	5·49 ,,
10.	Fluorenone-2-(1′)-azo-2′-naphthol-6′ : 8′-disulphonic acid.	D + G-acid (2-naphthol-6 : 8-disulphonic acid).	Deep scarlet red crystalline powder (hot alcohol); m.p. above 310°.	Moderately soluble in water, slightly in acetone, soluble in hot alcohol.	Dyeing properties unsatisfactory.	5·92	5·49 ,,

TABLE C.

Fluorenonylamide Derivatives.

Name.	Method of preparation. A + 2-aminofluorenone.	Analysis (nitrogen). Found.	Calc.
1. 2-Oxalylaminofluorenone (oxal-di-2-fluorenonylamide).	A + oxalyl chloride.	6·55	6·8 p.c.
2. 2-Phthalylaminofluorenone (phthalal-di-2-fluorenonyl amide).	A + phthalyl chloride.	5·79	5·88 ,,
3. 2-Carbonylaminofluorenone (2-difluorenonyl carbamide).	A + carbonyl chloride (toluene solution).	6·99	6·73 ,,
4. 2-Thiocarbonylaminofluorenone (2-difluorenony thiocarbamide).	A + thionyl chloride.	6·83	6·42 ,,
5. 2-Malonaminofluorenone (malon-di-2-fluorenonyl amide).	A + malonic acid and phosphorus pentachloride.	6·38	6·4 ,,
6. 2-Succinaminofluorenone (succin-di-2-fluorenonyl amide).	A + succinic acid and phosphorus pentachloride.	6·27	5·98 ,,
7. 2-Glutaraminofluorenone (glutar-di-2-fluorenonyl amide).	A + glutaric acid and phosphorus pentachloride.	5·96	5·76 ,,

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.

Received, July 13, 1931.

Influence of Amino-acids on the Hydrolysis of Starch by Cumbu Amylase.

By D. Narayanamurti and C. V. Ramaswami Ayyar.*

The influence of amino-acids on diastatic hydrolysis has been the subject of study by numerous investigators. Sherman (*J. Amer. Chem. Soc.*, 1921, **43**, 2461) in a series of investigations found that they had an accelerating action on the hydrolysis of starch by barley malt amylase. These results were confirmed by Patwardhan and Norris (*J. Indian Inst. Sci.*, 1928, **11A**, 121) but they failed to activate diastatic preparations from cholam. They found that hippuric acid alone had any accelerating influence, all the other amino-acids tried having an inhibiting action. Ohlson (*vide* Karrer, "Polymere Kohlenhydrate," 1925) reported inactivation. It has however been claimed by Haehn (*cf. Indian Inst. Sci.*, 1929, **12A**, 109) that amino-acids in combination with certain colloids can effect the hydrolysis of starch even in the absence of any enzyme material. We record here results of some experiments undertaken to examine this question.

Experimental.

The enzyme was prepared from malted cumbu as described in an earlier paper (Narayanamurti, Norris and Ayyar, *J. Indian Inst. Sci.*, 1929, **12A**, 105). Soluble starch (B. D. H., A.R.) and pure alanine (Kahlbaum) were used in these experiments.

Influence of Concentration of Alanine.—The influence of concentration of alanine on the activity of the enzyme was first investigated. The results are recorded in Table I.

TABLE I.

The reaction mixture was composed of 80 c.c. of 2·25 p.c. starch paste, 10 c. c. of alanine solution and 10 c. c. of enzyme solution.

Time in min.	Activity in c.c. of sodium thiosulphate for Concentration of alanine in reaction mixture in p.c.				
	0	0·0	0·05	0·1	0·2
30	1·5	1·5	1·6	1·7	2·0
125	3·9	4·2	4·6	4·7	4·7
180	5·0	5·5	5·8	6·0	6·0
240	5·9	6·5	6·9	7·0	7·0
300	6·8	7·2	7·8	7·8	8·0

It is evident from the table that the amino-acid has slight accelerating effect at all the concentrations studied. Closer examination of the results shows that the effect is not in proportion to the concentration of the amino-acid and suggests that probably it is a case of adsorption. It is probable that the alanine is adsorbed on the enzyme particle when it acts as a peptiser bringing more active centres or it may be that it simply acts as a protector thus preventing the destruction of the enzyme particle. In this connection we should mention that the experiments of Michaelis (Peters, *Trans. Faraday Soc.*, 1930, **26**, 803) and those of Peters (*ibid.*) indicate that monoamino-monocarboxylic acids are not adsorbed by neutral adsorbents. Our experiments on the influence of the amino-acid at the isoelectric point of the enzyme is also of interest.

Influence of Hydrogen-ion Concentration.—The foregoing experiments were done in unbuffered solutions. The effect was then tried at three different hydrogen-ion concentrations, *viz.*, optimum p_H, acid side of optimum p_H and alkaline side of optimum p_H. The results are given in Table II. It will be seen that the amino-acid is practically without any effect at the optimum p_H (*cf.* action of neutral salts, Narayanamurti, *J. Indian Inst. Sci.*, 1930, **13A**, 63) but has an accelerating action on both sides of the optimum p_H. The acceleration caused on the alkaline side is more pronounced and regular.

TABLE II.

The reaction mixture contained 70 c. c. of 2·5% starch paste, 10 c. c. of Walpole's acetate buffer of required p_H, 10 c. c. of alanine (containing 0·05 g.), 10 c. c. of enzyme solution and 5 c. c. of toluene. Temperature of the reaction was 30°.

Activity in c.c. of thiosulphate for

Time in min.	p_H, 6·02			Opt. p_H			p_H, 4·07		
	Control.	Alan.	Inc.	Control.	Alan.	Inc.	Control.	Alan.	Inc.
30	1·8	1·9	0·1	1·9	2·0	0·1	1·0	1·4	0·4
60	2·5	2·9	0·4	2·6	2·6	0·0	1·9	2·4	0·5
240	6·7	7·4	0·7	7·3	7·3	0·0	6·3	6·6	0·3
300	7·6	8·6	1·0	8·0	8·2	0·1	7·3	7·5	0·2
360	7·8	9·2	1·4	8·8	8·9	0·1	8·2	9·0	0·8

The isoelectric point of alanine is situated at p_H, 6·5 and it was interesting to carry out some experiments at that p_H and at another hydrogen-ion concentration on the alkaline side of it. The results are given in Table III.

TABLE III.

The reaction mixture was composed of 50 c.c. of starch paste (2·5 p.c.), 10 c.c. of buffer of required p_H, 20 c.c. water, 10 c.c. of enzyme solution and 0·1 g. of alanine dissolved in 10 c.c. of water and toluene 10 c.c. The temperature of the reaction was 35°.

Activity in c.c. of sodium thiosulphate for

Time in min.	p_H, 6·518		p_H, 7·36		Increase in activity	
	Control.	Alanine.	Control.	Alanine.	p_H, 6·518.	p_H, 7·36.
60	1·2	1·5	1·2	1·4	0·3	0·2
120	1·9	2·2	1·3	1·9	0·3	0·6
180	2·2	2·6	1·6	2·2	0·4	0·6
240	2·5	3·1	1·8	2·6	0·6	0·8
300	3·1	3·7	2·1	3·1	0·6	1·0
360	3·4	4·1	2·3	3·4	0·7	1·1

It is evident that there is activation at these hydrogen-ion concentration the activation caused being greater at p_H, 7·36 than at 6·518.

TABLE IV.

Influence on the Hydrolysis of Different Starches and Glycogen.

The reaction mixture contained 50 c.c. of starch solution (1 p.c.), water 5 c.c., 0·025 g. of alanine dissolved in 5 c.c. of water, and 10 c.c. of enzyme extract.

Variety of starch.	Activity in c.c. of sodium thiosulphate for					
	Without buffer		With buffer		Increase in activity	
	Control.	Alanine.	Control.	Alanine.	Without buffer.	With buffer.
Potato	0·6	1·4	1·5	2·0	0·8	0·5
Maize	1·5	1·7	1·6	2·0	0·2	0·4
Wheat	1·6	2·3	1·5	1·9	0·7	04
Rice	0·9	1·4	—	—	0·5	—

The enzyme extract had practically no action on Oyster glycogen.

Influence on the Liquefaction of Starch.—It is well known that the diastatic hydrolysis of starch proceeds in stages and it was shown by one of us (Narayanamurti and Norris, *J. Indian Inst. Sci.*, 1928, **11A**, 134) that the enzyme from cholam malt could be separated into two components by electro-osmosis. One of the components is responsible for the liquefaction of starch while the other effects saccharification. So it was interesting to investigate whether the amino-acid had any effect on the liquefaction. The results are given in Table V. It is evident that liquefaction also is accelerated by the amino-acid.

TABLE V.

The reaction mixture was composed of starch paste (70 c.c. 2·5 p.c.), 10 c.c. of alanine solution containing 0·05 g. of the amino-acid, 10 c.c. of water, 10 c c. of enzyme solution and 5 c.c. of toluene. Temperature of the reaction was 30°. Liquefaction was followed by

measuring the viscosity of the reaction mixture at frequent intervals with the help of an Ostwald viscometer.

Time in min.	Viscosity-flow in seconds. Control.	With alanine.	Time in min.	Viscosity.	
0	100	100	60	74·3	58·56
10	94·5	93·4	90	66·7	58·5
20	93·9	85·4	120	63·9	55·4
30	87·4	81·0	240	53·0	47·0
45	78·0	61·4	300	51·1	46·2

TABLE VI.

Experiments with other Amino-acids.

The reaction mixture contained 80 c.c. of 2·5 p.c. soluble starch paste, 1 c.c. of $M/10$- amino-acid, 10 c.c. of enzyme solution and 10 c.c. of toluene. Temperature of the reaction was 35°.

Time in min.	Activity in c.c. of thiosulphate for Control.	Alanine.	Tyrosine.	Ph. alanine.	Tryptophan.	Arginine.	Urea.
60	0.4	0·7	0·5	1·1	1·2	0·9	1·3
120	1·7	2·1	1 3	1·1	1·7	0·9	1·8
180	2·1	2·4	1·6	1·1	2·0	0·9	2·3
240	2·6	2·9	1·6	1·1	2·2	0·9	2·7
360	3·6	3·9	1·6	1·2	2·6	0·9	3·6

	Control.	Hippuric acid.	Glutamic acid.
60	0·4	1·2	1·4
120	1·7	1·4	1·8
180	2·1	1·6	2·2
240	2·6	1·8	2·6
360	3·6	2·2	3·1

Increase in activity.

Time in min.	Alanine.	Tyrosine.	Ph. alanine.	Tryptophane.	Arginine.	Urea.	Hipp. acid.	Gluta. acid.
60	0·3	0·1	0·7	0·8	0·5	0·0	0·8	1·0
120	0·4	−0·4	−0·6	—	−0·8	0·1	−0·3	0·1
180	0·3	−0·5	−1·0	−0·1	−1·2	0·2	−0·5	0·1
240	0·3	−1·0	−1·4	−0·4	−1·7	0·1	−0·8	0·0
360	0·3	−2·0	−2·4	−1·0	−2·7	0·0	−1·4	−0·5

* In all the above experiments blanks were run for the absorption of iodine by the amino-acids.

Mechanism of Activation.—Narayanamurti (*J. Indian Inst. Sci.*, 1930, **13A**, 68) has indicated that the hydrolysis of starch by amylase is greatest near the isoelectric point of the enzyme particle and his experiments on the influence of neutral salts in diastase suggest that the beneficial action is probably due to the lowering of the electrokinetic potential of the enzyme particle. The experiments of Narayanamurti and Ayyar with tyrosinase (*J. Indian Inst. Sci.*, 1929, **12A**,109; *Biochem. J.*, 1930, **24**, 1655) also lead to similar conclusions. So cataphoretic measurements were undertaken to see if by addition of alanine the charge on the enzyme particle is brought down to its isoelectric point. Preliminary experiments suggest that the charge is lowered by the addition of alanine—cathode and anode cell liquids showing the same activity. But it is necessary to extend the experiments under varying conditions before any definite conclusions can be arrived at.

Summary.

Alanine alone has a continued accelerating effect on the hydrolysis of starch by cumbu amylase. Urea has an accelerating action which gradually diminishes with time. In the case of the other amino-acids there appears to be initial activation followed by inhibition.

Department of Biochemistry,
Indian Institute of Science,
Bangalore.

Received June 30, 1930.

Constitution of Corchoritin—a New Crystalline Bitter from Jute-seeds.—Part I.*

By Nirmal Kumar Sen.

The occurrence of a second bitter which accompanies corchorin in alcoholic extract of *Corchorus capsularis* has been noted in a previous communication (*J. Indian Chem. Soc.*, 1930, 7, 905). A small quantity of the impure substance has been isolated by fractional crystallisation of the mother-liquor of corchorin and further work shows that it is, in reality, a mixture, and the material could be separated into a chloroform-soluble and a water-soluble portion. The chloroform extract after repeated concentration and precipitation with petroleum ether, and finally after several crytallisations from alcohol (animal charcoal) gave a product crystallising in long prisms which melted with effervescence at 218-20° after preliminary softening. The anhydrous product had the formula $C_{12}H_{18}O_3$ and $[\alpha]_D^{\cdot\cdot} = -35{\cdot}1°$ in 96 per cent. alcohol.

As the properties of the compound do not agree with those of any known compound of the same emperical formula, it is considered to be a new compound and has been termed corchoritin. The colour reactions and other properties of this substance are such as to suggest its identity with corchorin but unlike corchorin this new compound does not yield any hexose on hydrolysis and no furfural or methyl furfural is obtained from the substance on distillation with 12 per cent. hydrochloric acid and the failure of the Keller-Kiliani test shows the absence of any desoxy sugar. An interesting fact to which attention may be directed is that whereas corchorin is *dextro*rotatory, corchoritin is *laevo*rotatory.

It seems to be a member of the homologous series having the general formula $C_nH_{2n-6}O_3$ to which corchogenin, the aglucone of corchorin belongs. Its intimate relationship with corchogenin is made more striking by its common occurence with the parent substance of corchogenin in the same plant.

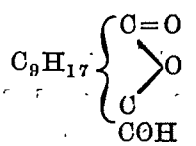
The presence of considerable amounts of reducing sugar in jute seeds considered in conjunction with ready hydrolysis of the bitters

* Communicated, in abstract to the Indian Science Congress, Nagpur, 1931.

by acids may also justify the conclusion that the primary glucosides are partly changed by fermerntative fission into secondary glucosides or to their aglucone. Further study of its still obscure chemistry is of interest since there is suspicion of its close relationship to the still little understood members of the jute bitters which according to Kobert (*Chem. Zentr.*, 1907, **1**, 1273) are cardiac poisons and may be placed pharmacologically in the list of digitaline group of substances.

The formation of monoacetate and a phenylurethane compound establishes the presence of a hydroxyl group. It contains no aldehydic, ketonic groupings or free carboxyl groups but is unsaturated and absorbs bromine and iodine and can be reduced to a dihydro-derivative. Ziesel's test shows the absence of any methyl group but the lactonic nature of the substance is established by its behaviour towards alkali and the slow titration of its alcoholic solution with aqueous alkali.

Thus, of the three oxygen atoms all have been accounted for, two by the lactonic group and one by an alcoholic group and this relationship may be shown by the following scheme:



The lactone dissolves in boiling alcoholic potash with much frothing and the resulting acid when liberated could not be isolated as such, but lost water forming an isomeric lactone along with yellow amorphous products evidently due to decomposition. The isomeric lactone possesses like corchoritin the formula $C_{12}H_{18}O_3$ and the formation of this substance may be either due to lactonisation on a hydroxyl group different from that involved in the lactone group of corchoritin or to the shifting of the olefinic linking. The exact mechanism is a subject for further investigation.

Although corchoritin does not give any positive reaction with ketonic or aldehydic reagents, nevertheless it was found to reduce Tollen's reagent promptly. An aromatic aldehyde group seemed out of the question although a tertiary aliphatic aldehyde might still have permitted the above behaviour. But in the deportment of this substance towards alkali, no positive evidence of a Cannizzaro reaction was obtained. This behaviour towards Tollen's reagent may be referable to unsaturated lactone group since Thiel (*Annalen*, 1901, **319**, 155) reported that the immediate reducing action on alkaline silver

solution is a characteristic property of $\triangle^{\beta\gamma}$ form whereas the $\triangle^{\alpha\beta}$ from develops a very faint colour which slowly deepens owing to gradual transformation of $\triangle^{\alpha\beta}$ into the $\triangle^{\beta\gamma}$ lactone. This test has given such uniform results with all of the substances studied by Jacobs and Hoffmann (*J. Biol. Chem.*, 1926, **67**, 333) that there appears to be complete justification in attributing the reduction of Tollen's reagents directly to the $\beta\gamma$-unsaturated lactone group. Although in its behaviour towards sodium nitroprusside (Jacobs and Hoffmann, *loc. cit.*) it proved to be an exception to the rule like bufagin, scillarin and the active substance of *Convallarea magels*; the significance of this failure to give a positive nitroprusside test cannot be evaluated in view of our meagre knowledge of the chemistry of these substanses.

Corchoritin is readily converted by strong hydrochloric acid into anhydrocorchoritin due to the removal of the hydroxyl group as water, since it no longer yields an acetyl compound.

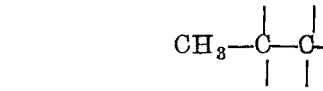
A large number of experiments have been made with the object of degrading corchoritin to simpler products in order to determine the nature of the ring structure present. When it was oxidised with potassium permanganate in alkaline solution after saponification of the lactone group, along with oxalic acid and acetic acid and other obscure amorphus products, a syrupy non-volatile acid which was identified as *pyro*racemic acid, was obtained.

Corchoritin when treated with nitric acid gives carbon dioxide, oxalic acid, and a small quantity of a yellow amorphous product. When subjected to dry distillation at a high temperature it undergoes decomposition at 100-10°/20 mm. It gives a bright yellow brittle microcrystalline mass ($C_{12}H_{16}O_2$) and a highly fluorescent thick oil of high boiling point from which a yellow solid, m.p. 110°, was obtained.

When fused with potassium hydroxide, corchoritin gives an acid (M.W. = 183), but no other definite product could be isolated.

On pyrogenic reduction with zinc dust in a current of hydrogen, corchoritin yielded a large volume of gaseous products and a brown semi-solid distillate from which a colourless substance was isolated possessing a characteristic naphthalene-like smell. It is unsaturated, absorbs bromine, gradually turns brown in air and reacts with explosive violence with fuming nitric acid forming a nitro-derivative. It also gives an orange-red picrate, m.p. 107°. Unfortunately, the yield of this substance was extremely small and it was not possible to investigate it further.

From the above experiments certain conclusions may now be drawn with regard to the structure of corchoritin. Since corchoritin contains only one double bond, the basic hydrocarbon is $C_{12}H_{24}$. This differs from the limit hydrocarbon by two hydrogen atoms and therefore it must be a cycloparaffin or cyclic limit hydrocarbon and is composed of at least one ring. The formation of pyruvic acid by the oxidation of corchoritin proves the presence of the group



as a part of the molecule.

It is hoped that further experiments may throw light on the constitution of this interesting substance.

Experimental.

Isolation of Corchoritin.—The combined resinous residue from the mother-liquor of corchorin was redissolved in alcohol and the fairly concentrated solution allowed to stand for some days. A small quantity of crystalline deposit mixed with yellowish brown gummy matter separated which was collected, washed with alcohol and dried on a porous plate. It was then extracted with hot chloroform, the operation requiring a large volume. The washed and dried extract was concentrated and was crystallised by the addition of petroleum ether, when it was obtained in aggregates of thin plates having a sulphur-yellow colour which could not be removed by recrystallisation from the above solvents. It was, however, finally obtained in pure form from dilute alcohol (50 p.c.) in the following manner.—

The substance (1·5 g.) was dissolved in 50 c.c, of hot 96 p.c. alcohol filtered several times through a bed of freshly heated active charcoal and the light yellow alcoholic filtrate was mixed with water (40 c.c.) and then warmed on the water-bath for a short time until the solution assumed a slight turbidity on cooling. It was then allowed to stand overnight. Radiating groups of lustrous prismatic needles began to separate, which were filtered, washed successively with dilute alcohol and water and dried in air (yield, 0·75 g.). It melts and effervesces at 218-20° with preliminary sintering at 130°. The crystals are different from those of corchorin and a mixture of the two showed a considerable depression of the melting point. For this substance the name corchoritin is proposed.

Corchoritin thus obtained is also extremely bitter. The air-dried product on analysis gave results which were different from those

given by the substance dehydrated in vacuum over phosphorus pentoxide at 110° or in an air-oven at 125°, the percentage of carbon being considerably lower in the former case. It was therefore inferred that the substance contains water of crystallisation. In order to verify the limit of stability of the attached water molecule, the air-dried material was first dried in a vacuum desiccator over concentrated sulphuric acid for a week until it was of constant weight. (0·9476 g. lost 0·002 g. water; H_2O, 0·21 per cent). By this treatment the bitter changed neither its colour nor its characteristic crystalline appearance. Finally a weighed quantity of the dried material was dehydrated in vacuum over phosphorus pentoxide in a toluene-bath until constant in weight with the following results:

TABLE I.

Substance taken = 0·5516 g. (dried for a week over conc. H_2SO_4).

Time of drying in hours.	Total water lost.	Percentage of water lost.
4	0·015 g.	2·71
8	0·0182	3·3

TABLE II

Substance taken = 0·4736 g. (air-dried).

2	0·011	2·3
4	0·0127	2·68
7	0·0184	3·88
10	0·0188	3·96

The material thus heated lost its crystalline structure but when heated in air-oven at 125-28° it turned light yellow and slight decomposition appeared to have taken place, although the melting point remained unaltered. When analysed the following results were obtained.

(1) Air-dried substance, dried in vacuum over P_2O_5 at 110° (Found: H_2O, 3·96. $C_{12}H_{18}O_3$, $\frac{1}{2}H_2O$ requires H_2O, 4·11 per cent.).

(2) Air-dried substance. (Found: C, 66·01; H, 8·8. $C_{12}H_{18}O_3$, $\frac{1}{2}H_2O$ requires C, 65·75; H, 8·67 per cent.).

(3) Anhydrous substance. (Found: C, 68·77; H, 8·94; M. W. (cryoscopic method in glacial acetic acid), 192. $C_{12}H_{18}O_3$ requires C, 68·57; H, 8·57 per cent., M. W., 210)

(4) Material dried in air-oven at 125-28° (light yellow slightly decomposed product). (Found: C, 71·3, 79·2; H, 8·25, 8·7 per cent.).

All these evidences lead to the conclusion that the compound invariably contains water of crystallisation which is very tenaciously held by the molecule and is only removed when dehydrated under reduced pressure but under the ordinary pressure the molecule suffered slight decomposition with the production of a yellow product.

The specific rotation of the anhydrous substance was observed in ethyl alcohol solution, $l=2$; $c=2·8912$; $a_D^{27}=-2·03$; $[a]_D^{27}=-35·1$.

Corchoritin is sparingly soluble in water and alcohol (50 p.c.) but readily soluble in hot chloroform, acetic acid, alcohol (95 p.c.), methyl alcohol and pyridine. It dissolves readily in cold concentrated hydrochloric acid and a yellow product is deposited on standing overnight. In glacial acetic acid it gives a beautiful red coloration with *o*-phenylenediamine and the reaction is so delicate that a trace of corchoritin can be detected by this means. It gives an intense yellow colour with ferric chlorlde in alcoholic solution. It dissolves in concentrated sulphuric acid with reddish-brown colour and a yellow substance separates out on the addition of water No derivatives of corchoritin with hydroxylamine, phenylhydrazine or semicarbazide could be obtained. Corchoritin contains no nitrogen, reduces Tollen's reagent (*J. Biol. Chem.*, 1926, **67**, 333) in the cold, decolourises permanganate and bromine water. It gives the following colour reactions.

(1) Liebermann's "Cholestol" reaction—(*cf.* Lewkowitch, *J. Soc. Chem. Ind.*, 1892, 11, 44). A small qnantity (0·25 g.) of the substance is dissolved in hot acetic anhydride (3 c.c.) filtered and the cold filtrate treated with a drop of concentrated snlphuric acid. It gives a transient violet pink coloration which immediately changes to beautiful deep green colour.

(2) Hagar-Salkowski reaction—(*Z. Physiol. Chem.*, 1908, **57**, 385). A small quantity of the substance is dissolved by heat in glacial acetic acid (0·1 g. in 3 c.c.) filtered and the filtrate mixed with 1 c.c. chloroform and then a few drops of concentrated sulphuric acid. A brownish-yellow colour develops which changes rapidly to green.

(8) Keller-Kiliani Test—negative, Keller (*Ber. Deut. pharm, Ges.*, 1895, **5**, 275). Only a brown colour is produced which changes to green when a small quantity of corchoritin is dissolved in acetic acid containing ferrous sulphate and a few drops of sulphuric acid added.

Acetylcorchoritin.—This was prepared by heating corchoritin (0·5 g.) with acetyl chloride (12 c.c.) on a water-bath for two hours. Excess of acetyl chloride was evaporated off and the product was poured into water slowly with constant stirring when a white flocculent precipitate was obtained. This was filtered, thoroughly washed with water and crystallised from dilute alcohol (80 p.c.), from which it is obtained in short course rods melting at 120-22°. It is *laevo* rotatory $[\alpha]_D^{28\cdot5} = -6\cdot8$. It is readily soluble in all ordinary solvents and is free from any bitter taste. (Found: C, 66·32; H, 8·1; acetyl (Perkin's method), 17·4. $C_{14}H_{20}O_4$ requires C, 66·6; H, 7·9; acetyl, 17·06 per cent.).

The *phenylurethane* of corchoritin was prepared by heating corchoritin suspended in an excess of phenylcarbamide. After half an hour a crystalline mass separated on cooling. It was washed several times with light petroleum ether and hot benzene to remove the excess of the reagent and finally recrystallised from dilute alcohol, from which it was obtained in shining plates melting at 254-66°. It was tasteless, sparingly soluble in benzene, alcohol and insoluble in light petroleum ether. The yield was very poor. (Found: N, 4·0. $C_{19}H_{23}O_4$ N requires N, 4·25 per cent.).

Iodine Value.—The iodine value of corchoritin was determined by Wij's method. Complete absorption of iodine was observed after 24 hours' contact (I. V., 136·05) while 1 to 2 hours contact gave lower results (I. V., 124·6), but in all cases an excess of iodine was absorbed over that indicated by one double bond, (Calc. I. V., 121·0).

The brown sticky mass left in the flask after the titration with sodium thiosulphate in the second experiment was separated and dissolved in carbon tetrachloride in which it was freely soluble. On evaporating off the solvent, an orange-yellow iodo-derivative was obtained which was well-washed with sodium thiosulphate and water and crystallised from dilute acetic acid from which it was obtained in canary yellow needles melting at 150°. It was soluble in chloroform, carbon tetrachloride and in glacial acetic acid.

Neutralisation Value of Corchoritin.—Although corchoritin is not acid to indicators, it neutralises alkalis but when saponified with al-

coholic caustic potash for a long time its titration presents difficulties owing to development of colour and decomposition.

The acid value was found to be 0·84 but on adding an excess of N/10- potassium hydroxide and allowing it to stand in the cold for two hours and titrating back, the alkali equivalent to acid value 113·4 was found to have been absorbed. In course of the titration it was found that the corchoritin solution after neutralisation with alkali gradually became deep red on standing for sometime apparently owing to the liberation of alkali. The explanation seems to be that the salt of the lactonic acid is gradually hydrolysed and the lactone is reformed liberating alkali.

Saponification Value.—This was determined by heating corchoritin with excess of 0·1*N*-alcoholic potash under reflux for 1 to 6 hours and titrating back the excess of alkali. Longer heating produces a dark coloured liquid which rendered titration impossible. The results are summarised in the following table.

TABLE III.

Anhydrous substance taken.	Time.	0·1*N*-KOH required.	Saponification value.
(1) 0·3264 g.	after 5 minutes (in the cold)	0·049 c.c.	0·84
(2) 0·3264	after 2 hours standing (in the cold)	6·6	113·4
(3) 0·4348	heated for 1 hour	12·75	164·5
(4) 0·3208	heated for 4 hours	10·15	177·5
(5) 0·2874	heated for 6 hours	10·05	196·2

The difference between the saponification and neutralisation value is very great and it thus becomes evident from the above table that it is partially converted into acid by heating with alcoholic caustic potash. Moreover, the soap solution obtained from experiment No. 3 yielded yellow amorphous product whose acid value was found to be 43·42. This proves that the lactone has been reformed to a considerable extent.

Action of Boiling Alcoholic Potash on Corchoritin.—Corchoritin (0·5 g.) was saponified by boiling in 25 c.c. of 0·1*N*-alkali and alcohol was evaporated off under reduced pressure and the yellow sparkling solution was acidified with acetic acid when a volumnious yellow

amorphous mass was separated. This was filtered and washed with water. The diluted filtrate on standing overnight deposited a white gelatinous mass which was collected, washed and dried in *vacuo* over concentrated sulphuric acid. The dried material was extremely hard and brittle. On recrystallisation from alcohol, it formed lustrous scales which melted with effervescence at 182°. It dissolved in methyl alcohol and less readily in alcohol and burnt with a smoky flame leaving no residue. Unlike corchoritin, the substance does not contain water of crystallisation and is tasteless but slowly develops a slight bitter taste towards the back of the tongue. It gives the Liebermann 'cholestol' reaction and in concentrated sulphuric acid develops the same red colour produced by corchoritin and it seems to be an isomeric lactone. The yield was too poor to admit of any further detailed study into the nature of the substance. (Found: C, 68·81; H, 8·75. $C_{12}H_{18}O_3$ requires C, 68·57; H, 8·57 per cent.).

The yellow residue dissolved in alkali from which it could be precipitated by acid. Attempts to crystallise the substance from various solvents were unsuccessful. A portion of the yellow substance when warmed with dilute hydrochloric acid and the product filtered through a bed of animal charcoal deposited a white crystalline substance which was found to be identical with corchoritin.

Action of Sodium Ethylate on Corchoritin.—Sodium (0·5 g.) was dissolved in absolute alcohol (10 c.c.) and corchoritin (0·5 g.) was added to the mixture. It dissolved with a red colour which gradually changed to brown. After heating for 4 hours on a sand-bath the product was poured in ice-water and 2 c.c. of ice-cooled glacial acetic acid were added. A yellowish-brown gelatinous precipitate separated, which was collected, washed and dried. When purified from dilute alcohol it was obtained as a deep yellow amorphous powder melting with decomposition at 208° with preliminary softening at 185°. It was tasteless and dissolved in alkali when warmed. The neutralised filtrate was extremely bitter to the taste showing that the reaction was not complete. It shows that isomeric change has taken place but attempts to isolate any crystalline substance from the highly coloured product were unsuccessful.

Anhydro-corchoritin.—Corchoritin (1·39 g.) dissolved at the ordinary temperature in hydrochloric acid (30 c.c., *d* 1·19). Solution readily occurred with a pink colour which gradually changed to dirty green. After about 15 minutes crystals began to separate. After

several hours the substance was collected and washed thoroughly with hot water until free from acid. It was then allowed to crystallise slowly from its ethereal solution in a desiccator over concentrated sulphuric acid in lustrous light yellow flakes, m. p. 97° (decomp.). It dissolved in almost all organic solvents. Attempts to acetylate, benzoylate and to prepare a phenylurethane derivative of the substance in the usual manner resulted in the recovery of the unchanged material. (Found: C, 74·78; H, 8·5; M.W., 180. $C_{12}H_{16}O_2$ requires C, 75·00; H, 8·33 per cent., M.W., 192).

The following experiment shows that the conversion of corchoritin into anhydro-corchoritin is quantitative. Corchoritin was dissolved in 10 c.c. of hydrochloric acid (*d* 1·19) and allowed to stand overnight in a corked flask. It was then diluted with 20 c.c. of water and heated under reflux. After 4 hours it was filtered through a weighed Gooch crucible, washed till free from acid and dried to constant weight in a vacuum desiccator over sulphuric acid [0·4779 g. gave 0·4050 g. anhydro-compound (insoluble) = 84·7 per cent.]. A further quantity (m.p. 98° decomp.) of 2·42 per cent. was isolated from the yellow filtrate by extracting with ether, thus giving a total yield of 87·12 per cent. ($C_{12}H_{18}O_3$, $\frac{1}{2}H_2O$ requires H_2O, 87·6 per cent.).

The filtrate was neutralised and treated with the combined carbonate-citrate reagent [Shaffer and Hartmann (micro-method), *J. Biol. Chem.*, 1921, **45**, 365] but only a trace of reducing sugar was obtained.

Action of Cold Concentrated Hydrochloric Acid on Corchoritin.—Finely powdered corchoritin (1 g.) was added to 30 c.c. of cooled hydrochloric acid (*d* 1·19). At first a portion of the substance separated but soon redissolved completely with a dirty green colour. The mixture was then kept overnight in contact with ice in a closed vessel. The dark yellow substance which separated was collected, washed with ice-cold hydrochloric acid and dried in a vacuum over solid caustic potash for 4 days when it was found to be free from adhering hydrochloric acid. The product was obtained in an amorphous condition, having in mass a greenish-yellow appearance. It was then purified from chloroform by the addition of petroleum ether in microcrystalline condition (yield, 0·7 g.). The melting point was not satisfactory and it shrinked at 68° and decomposed at 90°. The results of analysis, obtained were not satis-

factory after repeated trials. This is probably attributed to the admixture with the anhydro-compound. (Found: Cl, 13·2).

The mother-liquor could be almost completely precipitated by dilution with water and the material obtained in this way was found to be anhydro-corchoritin.

Distillation of Corchoritin with Hydrochloric Acid (12 p.c.).—When corchoritin (0·5 g.) was distilled with 12 p.c. hydrochloric acid (120 c.c.) according to the method of Willstätter at 130-60° in a glycerinebath, it changed into a yellow resinous product and the distillate gave no tests for furfural or methyl furfural by means of phloroglucinol. The aqueous-acid solution in the distilling flask on neutralisation and concentration yielded (*i*) a small quantity of a yellow product soluble in ether, (*ii*) did not reduce Fehling's solution, (*iii*) did not react with phenylhydrazine, the absence of glucose thus being indicated.

Action of o-*Phenylenediamine on Corchoritin.*—Corchoritin (0·42 g.) was dissolved in glacial acetic acid (20 c.c.) and heated for ½ hour with *o*-phenylenediamine hydrochloride (0·5 g.). A blood red coloration was produced. The mixture was concentrated and allowed to stand for several days but no crystalline substance separated. On pouring the red solution in a large volume of water a red precipitate was produced which was collected and purified from methyl alcohol as red powder which melted with decomposition at 130-42° and the product contains nitrogen. It could not be obtained sfficiently pure for analysis.

Fusion with Potassium Hydroxide.—Corchoritin (5 g.) was gradually added to potassium hydroxide (70 g.) and water (7 c.c.) at 120°; a vigorous reaction took place with much frothing and evolution of inflammable gases. The mass was finally heated at 200-20° for ½ hour. The cold melt was dissolved in water, acidified with concentrated hydrochloric acid, extracted with ether and the ethereal solution was washed with water and extracted three times with a strong solution of sodium bicarbonate. The sodium bicarbonate extract was concentrated and acidified with dilute hydrochloric acid when a sticky yellowish-brown mass separated which was again extracted with ether, dried and the ether evaporated. The brown mass thus obtained had a strong fatty odour. The analysis of its silver salt gave 183 (approx.) as the molecular weight (0·247 g. silver salt gave 0·092 g. Ag; taking it to be monobasic M.W., 182·9). It was not obtained in sufficient quantity for further examination.

The aqueous mother-liquor after extraction with ether contained oxalic acid (isolated as calcium salt).

The dark brown insoluble residue left after all these operations had a strong naphthalene-like odour but nothing definite could be isolated from the mass by repeated attempts at crystallisation.

Attempts at Reduction of Corchoritin by Zinc and Acetic Acid.—Zinc dust in small quantities was added to boiling solution of corchoritin (1 g.) in glacial acetic acid solution (25 c.c.) and the mixture heated for 3 hours. After filtrating from unchanged zinc dust, the filtrate was diluted with water when a colourless substance deposited slowly on standing in aggregates of nodular crystals which proved on examination to be the unchanged corchoritin.

Dihydrocorchoritin.—A solution of corchoritin (1 g.) in 30 c.c. of dilute methyl alcohol was hydrogenated by electrolytic hydrogen in presence of 5 c.c. of 1 p.c. palladious chloride and 15 c.c. of 2 p.c. gum arabic. In about 6 hours approximately 1 molecular equivalent of hydrogen was absorbed, after which the metal separated as a precipitate and absorption of hydrogen ceased. The mixture was evaporated to dryness and the residue was extracted with chloroform. The glassy residue from the chloroform extract was repeatedly extracted with cold absolute alcohol. The combined extract was concentrated and addition of water in the solution produced a white precipitate which was crystallised from dilute acetic acid in colourless needles, melting at 191°. It is tasteless and does not reduce Tollen's reagent nor absorbs bromine in chloroform solution showing that the double bond had been hydrogenated. (Found: C, 67·57; H, 9·51. $C_{12}H_{20}O_3$ requires C, 67·9 H, 9·4 per cent.). The same substance was obtained by reducing corchoritin in methyl alcoholic solution with sodium amalgam but the yield was very poor.

Action of Heat on Corchoritin.—When corchoritin (0·2 g.) was heated in a hard test tube at 220° in a glycerine-bath, it melted with effervescene and did not turn baryta milky but on raising the temperature, the substance gradually turned brown and carbon dioxide being evolved turned baryta milky. The substance partly sublimed to a yellow mass and a brown sticky liquid was found in the tube, which on cooling became hard and transparent. It was devoid of bitter taste and dissolved in oil of turpentine with a yellow colour. With acetic anhydride and concentrated sulphuric acid it first gave a fugitive reddish-brown colour which immediately changed to green and finally yellow on standing.

Distillation under Reduced Pressure.—Corchoritin (5 g.) was distilled at 20 mm. in a small distilling flask. The temperature was raised slowly, and there was much evolution of gas and a sulphur-yellow liquid came over between 90° and 110°, which condensed as a crystalline mass in the receiver. A strongly flourescent oil having a very high boiling point was left in the distilling flask which solidified on cooling to a hard brittle resinous mass from which a yellow solid, m.p. 110°, was obtained by shaking the ethereal extract of the resin with caustic soda.

The sublimate was collected and on examination was found to be the anhydro-corchoritin.

Pyrogenic Reduction with Zinc Dust.—Corchoritin (5 g.) was distilled with zinc dust in the usual way in a stream of hydrogen. Gaseous products were evolved. The results of examination are recorded in Table IV. The brown distillate which was collected in the receiver, cooled in a freezing mixture consisted of a mixture of solid and liquid having a strong naphthalene-like odour which turned deep brown on standing in air. The liquid was absorbed in a porous plate and the crude product decolourised potassium permanganate, absorbed bromine in carbon tetrachloride solution and dissolved in fuming nitric acid with explosive violence. The solid crystallised from alcohol yielded a very small quantity of glistening colourless needles melting at 135°. It yielded an orange-red picrate, m.p. 107°. On nitration with fuming nitric acid, it yielded a yellow compound, probably a nitro-derivative, which when purified from acetic acid, melted with effervescence at 150°. (Found: N, 10·35 per cent).

TABLE IV

Total volume of gas collected = 460 c.c. out of which 60 c.c. were analysed and the results gave the mean of several experiments.

Gas.	Volume in c.c.	Per cent.
Carbon dioxide	2.8	4.66
Hydrocarbon (C_nH_{2n})	1.0	1.66
Oxygen	1.4	2.31
Carbonmonoxide	4.8	8.00
Methane	1.4	2.31
Hydrogen	48.6	81.00
	60.00	99.94

Action of Oxidising Agents on Corchoritin.

(a) *Alkaline potassium permanganate.*—A solution of 0·73 g. of the substance in 30 c.c $N/2$-alcoholic caustic potash was refluxed for four hours. The soap solution after distilling off the alcohol under reduced pressure was treated with 150 c.c. of 3 per cent. potassium permanganate. Oxidation occurred slowly in the cold with gradual deposition of manganese dioxide. The solution was filtered, concentrated to a small volume and when acidified it yielded no solid product. The whole was repeatedly shaken with ether and the ethereal solution was washed, dried and on evaporation, yielded a glassy viscous mass having an acid smell of acetic acid, which did not solidify even on standing over sulphuric acid in a vacuum desiccator for a month. It was purified by redissolving in ammonia, acidifying and extracting with ether. It had a strong acid reaction on litmus and its neutral solution did not give any coloration with ferric chloride and did not react with acetic anhydride or acetyl chloride. It reduced Fehling's solution promptly and gave a positive iodoform reaction with alkaline iodine solution depositing iodoform on standing. It was readily identified as pyruvic acid through its *p*-nitrophenylhydrazone m. p. 220°. The aqueous mother-liquor after extraction with ether contained oxalic acid (isolated as calcium salt).

(b) *Dilute nitric acid.*—0.5 G. of the substance and 5 c.c. of nitric acid (d 1·36) were taken in a boiling tube provided with a delivery tube that dipped in a clear baryta water. The whole was heated on a water-bath at 60°. The baryta turned turbid gradually and deposited barium carbonate and the reaction mixture gradually turned yellow. After six hours, it was poured in a beaker and slowly heated on the water-bath, adding water from time to time and with an occasional shaking. A deep yellow solution was obtained, which was extracted with ether. The washed and dried ethereal solution on evaporation deposited a yellow viscous mass which on standing partially solidified to a beautiful crystalline mass. Almost colourless needles were collected, washed with a little water and on examination they were found to be oxalic acid. The yellow gummy mass could not be identified owing to the small quantity of the substance available.

(c) *Kiliani-chromic acid solution.*—A solution of the substance (0.7 g) in acetic acid (10 c.c.) was treated with 3 c.c. of Kiliani-chromic acid solution. Oxidation was prompt and after five minutes

the mixture which contained excess of the reagent, was diluted with water and the whole allowed to stand overnight when an unidentified yellow acid gradually separated. It could not be crystallised from the ordinary solvents, in which it was insoluble. It decomposed with charring at 240° with preliminary sintering at 215°. The substance could not be obtained sufficiently pure for analysis.

The author wishes to express his grateful thanks to Professors J. C. Ghosh and S. N. Bose for their keen interest in this investigation and also to the Indian Chemical Society for a grant which has partly covered the cost of this research.

He also takes this opportunity of expressing his gratitude to Messrs Bengal Chemical and Pharmaceutical Works Ltd. Calcutta, for kindly extracting a large quantity of the seeds for the author.

CHEMICAL LABORATORY,
UNIVERSITY OF DACCA.

Received June 22, 1931.

Chemical Examination of the Roots of *Rauwolfia Serpentina*, Benth.

By Salimuzzaman Siddiqui and Rafat Hussain Siddiqui.

Rauwolfia Serpentina, Benth, (Hindi, Chhota-chand, Sanskrit, Chandrika or Sarpagandha) is a short shrub inhabiting the moist and hot regions of India. Its roots, which are crooked, tapering and $\frac{1}{4}''$ to $\frac{1}{2}''$ in diameter in thickness, are mentioned in older literature as a febrifuge, a remedy for snake-bites and a cure for dysentery and other painful affections of the intestines. In comparatively later times the drug has gained the reputation of being a general sedative and a cure for certain types of insanity.

The chemical work so far done on the drug was limited to the detection of an alkaloidal principle in the roots by Dymock and coworkers ("Pharmacographia Indica," Vol. II. p. 415), who also noted the presence of a yellow resin and a trace of a wax. As a result of our investigations we have obtained a total alkaloidal yield of 0·5 p.c. on the weight of the dry powered root, and isolated out of it five crystalline alkaloids, which appear to be new from their general characteristics and could be classed into the following two the groups:—

A. The *Ajmaline group*, (so named by us in memory of the late Hakim Ajmal Khan, the founder of this Institute) consists of three white, crystalline, weaker bases:

(*i*) Ajmaline ($C_{20}H_{26}O_2N_2$), m.p. 158-60°; 0·1 p.c. on the wt. dry powered root,

(*ii*) Ajmalinine ($C_{20}H_{23}O_4N$), m.p. 180-81°; 0·05 p.c. ,,

(*iii*) Ajmalicine —— m.p. 250-52° (decomp.); 0·02 p.c. ,,

and an amorphous cream-coloured alkaloidal residue, forming about a quarter of the total alkaloidal yield, which is under further investigation.

B. The *Serpentine group*, consists of two bright yellow, crystalline stronger bases:

(*i*) Serpentine ($C_{21}H_{23}O_4N$), m.p. 153-54°; 0·08 p.c. on the wt. of dry powdered root.

(*ii*) Serpentinine —— m.p. 263-65° (decomp.); ,,

and about 0·08 p.c. of a reddish-yellow uncrystallisable alkalodial residue.

The method of separation of the alkaloids was chiefly based on the differences in the strength of the bases, on the one hand, and the solubilities of their hydrochlorides, on the other. Thus while the white group of the bases is completely precipitated from the aqeuous solutions of its salts by dilute ammonia, a quantitative liberation of the serpentine group is possible only on addition of a strong solution of sodium hydroxide. Of the hydrochlorides of the bases, ajmaline hydrochloride is difficultly soluble in cold water and 10 p.c. aqueous or alcholic hydrochloric acid, the hydrochlorides of ajmalinine and ajmalicine and the uncrystallised white alkaloid though varying in their solubilities in these solvents when pure, are together, easily soluble in them; and the hydrochlorides of the serpentine group are soluble in water and 10 p.c. alcoholic hydrochloric acid but insoluble in 10 p.c. aqueous hydrochloric acid.

The separation of ajmalinine and ajmalicine presented great difficulties and was possible only on a careful fractional precipitation of the bases by gradual addition of water to the alcoholic solution of the alkaloidal residue left after the isolation of ajmaline, ajmalinine being more soluble in a mixture of alcohol and water than ajmalicine but less soluble than the uncrystallised white base. Apart from the aikaloids we also isolated:

1. A *phytosterol*, $C_{30}H_{48}O_2$, melting at 159-60°, and showing $[\alpha]_D^{33} = -68{\cdot}5°$ in 1·3 p.c. chloroform solution, which we consider to be identical with mykosterin ($C_{30}H_{48}O_2$), m.p. 159-60°; $[\alpha]_D$ = $-129{\cdot}29°$, $-129{\cdot}5°$, but have, owing to the so far unaccountable difference in the optical rotatory power of the two compounds, provisionally called serposterin.

2. Oleic acid and a saturated acid melting at 58°, which is probably a mixture of stearic and palmitic acids.

3. A mixture of unsaturated alcohols corresponding to the formula $C_{25}H_{44}O_2$, which did not give any uniform product; and noted the presence of a resinous acid and a neutral resin which were not investigated further.

Pharmacological actions.—A series of preliminary experiments on frogs showed, that from the stand-point of physiological action also the white and the yellow bases form two distinct groups, the former acting as a general depressant of heart, respiration and nerves, and the latter as a paralyser of respiration and depressant of nerves, but a stimulant of the heart. The lethal dose of serpentine group of alkaloids

was found to be the same as that of the ajmaline group in case of frogs *vis.*, 0·5 g. per kg. weight of the body, but it was about four times higher for rats, being 0·05 g. per kg. body weight for serpentine and 1·2 g. per kg. body weight (12 g. for an adult human being) in case of ajmaline. In constrast to the lethal dose the minimum therapeutic dose of ajmaline, fixed on the basis of the dose of the crude drug and found effective by experience as a general sedative and hypnotic, is remarkably low, being only 0·005 to 0·01 g. for an adult. Clinical observations in respect of this as well as the other bases are in progress and the highly favourable results obtained in case of acute insomnia accompanied with fits of insanity promise it to form a valuable contribution to the list of existing sedatives.

Experimental.

The material used was obtained from the Patna markets by one of us personally and identified by the Sibpur Botanical Institute, Calcutta.

In illustration of the method worked out after a series of preliminary experiments for the separation of the different constituents, 5 kg. of well powdered drug were percolated six times with 90 p.c. alcohol, and the alcohol distilled off from the combined percolates under reduced pressure below 50°, till a thick greenish brown liquid was left behind. On complete removal of the solvent from an aliquot fraction of this liquid a semi-solid bitter extract was obtained, which was calculated out to form 10 p.c. of the weight of the dry roots. The total quantity of the crude extract was shaken out repeatedly with petroleum ether and then carefully concentrated further in *vacuo* till nearly all the solvent was removed. The light brown semi-solid extract was first treated with ammonia and then with caustic soda and extracted each time to exhaustion with ether containing a little alcohol. The alcoholic extract of the roots was thus subdivided into four fractions, the two middle, ethereal fractions constituting chiefly the alkaloidal contents (I), and the petroleum ether fraction and the final residue, the non alkaloidal contents (II).

I. The Alkaloidal Contents.

Separation of Ajmaline and Sepentine Groups.—The greenish ethereal solution obtained on treating the alcoholic extract with

ammonia and exhausting it with ether, was neutralised with acetic acid and freed of the solvent on the water-bath. The yellowish-brown paste, left behind as residue, was repeatedly digested with 5 per cent. acetic acid till all, except a little petroleum ether soluble residue, went into solution. The acetic acid solution was nearly neutralised with ammonia, the little dirty brown precipitate which was thereby produced was filtered off, and 15 per cent. hydrochloric acid added on to the filtrate under good cooling and shaking till no fresh precipitate formed on further addition of the acid. The hydrochloride precipitate (S) was filtered, washed with 10 per cent. warm hydrochloric acid and dried, and the reddish-yellow filtrate made alkaline with ammonia under good cooling. The copious cream coloured granular precipitate, which came down, was filtered, well washed and dried on a porous plate. The filtrate when shaken out with ether yielded a further small quantity of cream white bases from the ethereal layer (total yield 18 g.; 0·36 per cent. on the weight of the root).

The second ethereal fraction from the alcoholic extract containing the stronger bases was saturated with hydrochloric acid gas and the reddish-brown surupy precipitate of hydrochlorides, thereby obtained, was dissolved in hot water and filtered. The filtrate was made alkaline with ammonia and the small quantity of yellowish-white precipitate, which came down was worked up along with the first ethereal fraction of the alcoholic extract. The reddish-yellow filtrate from the precipitate gave a brilliant yellow flocculent precipitate, consisting chiefly of serpentine, on addition of a concentrated solution of caustic soda. The orange-coloured powder obtained on washing and drying the precipitate weighed 5 g. and along with the base from the hydrochloride precipitate (S), noted in the preceeding paragraph, constituted the total yield, 9·5 g (0·2 per cent. of the serpentine group of alkaloids).

Isolation of the Alkaloids of the Ajmaline Group.

(i) *Ajmaline.*—The cream coloured amorphous powder constituting the total alkaloids of the white group (18 g.) was dissolved in the least quantity of alcohol and ether (eventually also a little petroleum ether) added to the alcoholic solution to precipitate the impurities, which settled down as a dark brown paste. The light red filtrate was treated with ethereal hydrochloric acid till the bases were

completely precipitated as hydrochlorides. These were dissolved in the least quantity of a mixture of concentrated hydrochloric acid and 90 per cent. alcohol (1 : 8) and put in an ice-chest. The white crystalline powder of ajmaline hydrochloride which soon began to separate out, was filtered after a day, washed with a little alcohol and dried. It weighed 5·5 g. nearly (one third of the total yield of the ajmaline group) and after recrystallisation from the same medium melted at 133-34°. On addition of dilute ammonia to the aqueous solutions of the hydrochloride ajmaline was precipitated as snow white flocks, which when washed and dried formed a white amorphous powder melting at 158-60°. On slowly cooling a solution of the amorphous base in moist ethyl acetate, ajmaline crystallised out in large rectangular plates melting at 158-60° (yield 4·8 g.; about 0·1 per cent. on the weight of the root).

(*ii*) *Ajmalinine and* (*iii*) *Ajmalicine*.—The mother-liquor from ajmaline hydrochloride was diluted with water and made alkaline under ice-cooling with ammonia, which precipitated the remaining bases. These were washed and dried and once more purified by dissolving in alcohol and precipitating the impurities with ether and petroleum ether. The pale, straw coloured treacle left on removal of the solvents from the solution of the purified bases, was dissolved in absolute alcohol and the bases fractionally precipitated with water. After several repetitions of this process two fractions of nearly colourless, silky looking crystalline bases and a third fraction of an amorphous, cream coloured base were finally obtained. On crystallisation out of moist ethyl acetate, the first fraction yielded 1 g. of ajmalicine (0·02 per cent. on the weight of the roots) melting at 250-52° (decomp.) and the second fraction yielded ajmalinine (2·5 g., 0·05 per cent. of the roots), m.p. 180-81°. The third fraction weighed nearly 6·5 g. (0·13 per cent.) and could not be induced to yield any further crystalline base.

Isolation of the Alkaloids of the Serpentine Group.

(*i*) *Serpentine*.—The crude yellow alkalolds (9·5 g.) was dissolved in a little alcohol and ether added to the solution till no dark precipitate was formed on fresh addition of a little ether. The bright yellow ethereal solution of the purified bases was treated with hydrochloric acid gas and the reddish-yellow oily precipitate of hydrochloride, thus obtained, was dissolved in hot water and the bases

fractionally precipitated from the solution by ammonia and sodium hydroxide under ice-cooling, whereby a fraction of comparatively weaker, and another of strong, yellow bases were obtained. The latter fraction when dissolved in hot absolute alcohol yielded serpentine on slowly cooling the alcoholic solution as brilliant yellow, prismatic rods and plates melting at 153-54° (yield 4 g.; 0·08 per cent. on the wt. of the root). The mother-liquor yielded 1·5 g. (0·02 per cent.) of a reddish-yellow base, which could not be crystallised.

(*ii*) *Serpentinine.*—The fraction of the weaker yellow bases did not yield any crystal out of its solution in absolute alcohol even on long standing in the cold, but on addition of water to it till faint turbidity and slowly cooling in the ice-chest, serpentinine crystallised out in broad needles, which when filtered, washed with 60 per cent. alcohol and dried in air melted at 263-65° (decomp.) (yield 1 g.; 0·02 per cent. on the weight of the roots). The mother-liquor from serpentinine yielded a reddish-yellow amorphous powder on removal of the solvent, from which no further crystalline base could be isolated and which weighed 2·5 g. (0·05 per cent. on the roots).

Characterisation of the Alkaloids and their Salts.

Ajmaline, $C_{20}H_{26}O_2N_2$.—It is white when amorphous and forms rectangular prismatic plates with a light tinge of amber on crystallisation out of moist ethyl acetate (Plate I). The crystalline base swells up at about 110° giving off its water of crystallisation, begins to soften at 150° and melts at 158-60°. It is easily soluble in alcohol, ethyl acetate and chloroform, sparingly soluble in ether and benzene. In 1 p.c. chloroform solution it showed $[\alpha]_D^{33} = +128°$. The air-dried crystals of ajmaline lost 15·1 p.c. on drying to constant weight over P_2O_5 in *vacuo* at 100°, which would signify 3 molecules of water of crystallisation. $C_{20}H_{26}O_2N_2,3H_2O$ requires H_2O, 14·2 p. c. [Found: (the dehydrated base) C, 73·0; H, 8·12; N, 8·8. $C_{20}H_{26}O_2N_2$ requires C, 73·6; H, 8·0; N, 8·6 per cent.). Though containing two nitrogen atoms ajmaline is a monoacid base and forms only one series of salts.

Ajmaline Hydrochloride.—The hydrochloride of ajmaline, when prepared by adding ethereal hydrochloric acid in an alcohol-ether solution of the base, is a white amorphous powder which melts at 253-55° without blackening. On dissolving it in hot water and slowly cooling the solution, it crystallises out with 2 molecules of

water in large, ambercoloured rhombohedral prisms or aggregates in very characterististic eight or multipetalled flowers, melting sharply at 133-34°. The air-dried crystals lost 9·1 p. c. water on drying to constant weight over P_2O_5 in *vacuo* at 100° and then melted at 253-55°. $C_{20}H_{26}N_2O_2 \cdot HCl, 2H_2O$ requires H_2O, 9·0 p. c. [Found: (dry hydrochloride) N, 7·3; Cl, 9·6. $C_{20}H_{26}O_2N_2 \cdot HCl$ requires N,7·7; Cl, 9·8 per cent.). In 1 p.c. aqueous solution it showed $[\alpha]_D^{40} = +84·63°$

Ajmaline chloroplatinate was obtained on addition of 10 p.c. platinic chloride to a concentrated solution of ajmaline hydrochloride under good cooling. It is easily soluble in alcohol, difficultly in water and melts at 217-18°. [Found: Pt, 17·9. $(C_{20}H_{26}O_2N_2 \cdot HCl)_2 \cdot PtCl_4$ requires Pt, 18·4 per cent.].

Ajmaline picrate, prepared by adding dry ethereal picric acid to an alcohol-ether solution of the base, formed a bright yellow semicrystalline powder, which was easily soluble in hot, difficultly in cold water and alcohol and crystallised out of the latter in rectangular plates melting at 126-27°. After drying to constant weight in *vacuo* at 100° the anhydrous picrate melted sharply at 223°.

The gold salt of ajmaline could not be obtained, as gold chloride is readily reduced by ajmaline as well as all the other bases of the two groups. Colour reactions of ajmaline and other bases are shown in Table I.

Ajmalinine, $C_{20}H_{23}O_4N$.—It crystallises in nearly colourless hexagonal prisms out of moist ethyl acetate (Plate II) melting at 180-81°, is easily soluble in alcohol, chloroform, sparingly soluble in ether and benzene and insoluble in petroleum ether. $[\alpha]_D^{33} = -97°$. It contains one molocule of water of crystallisation, the loss of weight being 4·6 p. c. $C_{20}H_{23}O_4N, 1H_2O$ requires H_2O, 5·0 p.c. [Found: (dehydrated base) C, 70·4; H, 7·1; N, 5·50 $C_{20}H_{23}O_4N$ requires C, 70·4; H, 6·7; N, 4·1 per cent.).

Ajmalinine hydrochloride prepared by slowly adding dry ethereal hydrochloric acid to its alcohol-ether solution forms a white semicrystalline powder, which is soluble in alcohol as well as in water, shrinks at 213°, swells up at 235° and melts at 240-45° (decomp.). [Found: Cl, 9·1. $C_{20}H_{23}O_4N \cdot HCl$ requires Cl, 9·4 per cent.). $[\alpha]_D^{40} = -44°$ (1 p. c. aqueous solution).

Ajmalinine chloroplatinate prepared in the same way as ajmaline chloroplatinate formed an amorphous powder. It is easily soluble

PLATE I.

Ajmaline

(from moist ethyl acetate).

PLATE II.

Ajmalinine

(from moist ethyl acetate).

PLATE III.

Ajmalicine

(from moist ethyl acetate).

PLATE IV.

Serpentine

(from 99·4 % alcohol).

in alcohol and water m.p. 254-58° (decomp.). [Found: Pt, 18·1. $(C_{20}H_{23}O_4N\cdot HCl)_2PtCl_4$ requires Pt, 17·9 per cent.].

Ajmalinine picrate prepared in the same manner as ajmaline picrate, formed a bright yellow powder, which is easily soluble in alcohol and difficultly in water, softens at 175° and melts at 200-5°.

Ajmalicine.—It crystallises out of alcohol and water in colourless silky needles and out of moist ethyl acetate in long prismatic plates (Plate III) melting at 250-52° (decomp.). It is soluble in alcohol and chloroform, sparingly soluble in ether and benzene and insoluble in petroleum ether.

Ajmalicine Hydrochloride and Picrate.—Its hydrochloride and picrate, prepared as in the case of ajmalinine, formed white and bright yellow powders respectively. The *hydrochloride* was very sparingly soluble even in hot water, but easily in alcohol. It shrinks at 250° and melts at 260-63° (decomp.). The *picrate* is easily soluble in alcohol, difficultly soluble in water and melts at 212-15° (decomp.). Owing to the small quantity of the substance at our disposal the elementary analysis of the base and its salts could not be undertaken at present.

Serpentine, $C_{21}H_{23}O_4N$.—It crystallises out of 99·4 p. c. alcohol in bright yellow well defined prismatic plates (Plate IV) containing one molecule of water and melting at 153-54°. It is soluble in chloroform but is transformed by it on heating to a dark brown uncrystallisable powder melting at 245°. It is very sparingly soluble in alcohol when crystalline but easily so while amorphous, difficultly soluble in benzene and ether and insoluble in petroleum ether. It does not pass any light even in 0·5 p.c. chloroform solution, but its hydrochloride showed in 1 p.c. aqueous solution $[\alpha]_D^{40} = +188°$. The air-dried crystals when dried to constant weight in *vacuo* at 100 lost 7·0 p. c. of their weight. $C_{21}H_{23}O_4N + 1\frac{1}{2}H_2O$ requires H_2O, 7·1. [Found: (*Anhydrous salt*) C, 71·38; H, 6·3; N ; 3·4. $C_{21}H_{23}O_4N$ requires C, 71·4; H, 6·5; N, 4·0 per cent.).

Serpentine hydrochloride prepared by adding dry ethereal hydrochloric acid to a chloroform-ether solution of the base forms a cream coloured amorphous powder, which shrinks at 240° and melts at 260-61° (decomp.). (Found: Cl, 9·18. $C_{21}H_{23}O_4N\cdot HCl$ requires Cl, 9·10 per cent.). The hydrated form separates from hot water as tufts of needles, m.p. 133-35°.

Serpentine chloroplatinate formed a pale yellow amorphous powder, which is soluble in alcohol and water, and crystallises out of

the latter in long needles, m.p. 217-20° under blackening. [Found: Pt,. 17·9. $(C_{21}H_{23}O_4N\cdot HCl)_2\cdot PtCl_4$ requires Pt, 17·5 per cent.].

Serpentine picrate obtained by adding ethereal picric acid to a chloroform-ether solution of the base, formed a yellow amorphous powder, m.p. 261-62° (decomp.). It is easily soluble in warm alcohol, difficultly in cold alcohol and water.

Serpentinine.—It crystallises in brilliant yellow prismatic rods out of dilute alcohol, m.p. 263-65°. It is also easily soluble in ethyl acetate and chloroform, sparingly soluble in benzene and ether and insoluble in petroleum ether and water.

Serpentinine hydrochloride prepared by adding ethereal hydrochloric acid to the alcohol-ether solution of the base is a creamcoloured amorphous powder, and is soluble in alcohol and water m.p. 260-62°.

Serpentinine chloroplatinate is a yellow amorphous powder, soluble in alcohol, difficultly soluble in water, m.p. 260-263° (decomp.).

Serpentinine picrate prepared by adding ethereal hydrochloric acid to the alcohol-ether solution of the base, forms a bright yellow powder, which is easily soluble in alcohol but sparingly soluble in water, m.p. 225-27°.

The elementary analyses of serpentinine could not yet be undertaken owing to lack of a sufficient quantity of the substance.

II A. The Non-Alkaloidal Contents.

Examination of the Petroleum Ether Extract (A) Serposterin, $C_{30}H_{48}O_2$.—The petroleumether soluble portion of the alcoholic extract of the roots was repeatedly shaken out with water in ethereal solution to completely remove any salts of the alkaloids, dried over anhydrous sodium sulphate and freed of the solvent on the water-bath. The thick, dark green, liquid residue (25 g., 0·5 p.c. of the roots) was dissolved in 95 p.c. alcohol and kept for several days in the ice-chest. The light crystalline mass which separated out was carefully filtered in the cold, washed with cold alcohol and brought on a porous plate. The soft slightly greenish-white powder thereby obtained weighed 3 g. (·06 p.c. of the roots); and melted at 125°. After repeated crystallisation out of the same medium, a snow white silky crystalline mass was obtained which melted sharply at 159-60°, the melting point remaining unchanged on subsequent crystallisations. It had $[\alpha]_D^{33} = -68·5°$ (1·3 p.c. in chloroform). (Found: C, 81·82; H, 11·18. $C_{30}H_{48}O_2$ re-

quires C, 81·81 ; H, 10·9 per cent.). Mykosterin melts at 159-60° and shows $[\alpha]_D = -129·2, -129·5°$.

Examination of the Waxy Matter.—20 G. of the waxy matter left after removal of the solvent from the mother-liquor of serposterin were saponified with alcoholic potash, the alcohol evaporated off and the residue extracted with ether, then acidified with dilute hydrochloric acid and again extracted with ether. On drying over anhydrous sodium sulphate and removing the solvent on the water-bath the first ethereal solution yielded about 8 g. of the acid portion (*a*), and the second ethereal solutiun 7 g. of a dark green non-acidic odorescent liquid, (*b*).

Acid Fraction (*a*).—8 G. of this were converted into the barium salt in the usual manner to remove the non-acid impurities, the acid recovered from the salt and distilled under reduced pressure, whereby nearly all except about 2 g. of a dark brown residue distilled over at 190-94°/3·5 mm. as a nearly colourless liquid which congealed at about 20° to a white fatty mass. (Found: C, 77·3; H, 12·11. Oleic acid, $C_{18}H_{34}O_2$, distils at 285·5-286°/100 mm., congeals at 16° and requires C, 76·6; H, 12·1 p.c.; stearic acid distils at 291°/100 mm. melts at 69·6° and requires C, 76·0; H, 12·7 per cent.).

Saturated Acid.—The distilled acid was converted into the ammonium salt by passing ammonia into its ethereal solution and the ammonium salt dissolved in a very small quantity of absolute alcohol and kept in the ice-chest. The white crystalline ammonium salt, which separated out, was carefully filtered in the cold, washed with cold alcohol, and then extracted with a little ethereal hydrochloric acid. The acid obtained from the ethereal solution congealed at ordinary temperature and crystallised out of absolute alcohol, m. p. 58° (0·5 g.). Owing to lack of sufficient quantity further examination of the acid could not be undertaken.

Unsaturated Acid.—The mother-liquor from the ammonium salt of the above acid yielded about 2·5 g. of unsaturated acid, which congealed at about 15°, showed $n_D^{36} = 1·4455$ and appeared to be chiefly oleic acid.

Reduction of Unsaturated Acid.—To 1 g. of the above liquid acid in absolute alcohol (2 c.c.) was added platinum black (1 g.) prepared according to the method of Wilstätter and Meyer (*Ber.*, 1908, **41**, 1475, 2200), and the mixture was placed in a well-closed bottle

attached to a hydrogen generator and shaken in a shaking machine till absorption ceased. The resulting product was filtered from the platinum black and the filtrate cooled in the ice-chest. The white crystalline solid (about 1 g.) which separated out melted at 69° after recrystallisation out of absolute alcohol and showed no depression in its melting point when mixed with pure stearic acid.

Fraction (b), Alcohols.—The odorescent, dark green, non-acidic liquid (*b*), (7 g.) was easily soluble in all the organic solvents and failed to give any crystalline product even on acetylation. Consequently it was subjected to distillation under reduced pressure when it yielded about 2 g. of a reddish-yellow liquid at 150-70°/3 mm. The product, thus obtained, took up bromine in chloroform solution at 0°. (Found: C, 79·9; H, 11·65. $C_{25}H_{44}O_2$ requires C, 79·8; H, 11·7 per cent.).

II (B). The Alkaline, Ether-insoluble Portion of Alcoholic Extract.

The Acid and Neutral Resins.—The alkaline residue left after ethereal extractions of the alcoholic extract of the roots was digested with hot water, which dissolved nearly all except about 4 g. of a reddish-brown resinous product, which was insoluble in acids as well as in alkalis, soluble in alcohol but insoluble in all other organic solvents. The filtrate from this neutral resin gave a dark brown slimy precipitate on acidifying with dilute hydrochloric acid, which formed a chocolate coloured powder on drying (5 g.). The resinous acid thus obtained was soluble in alcohol but insoluble in all other organic solvents.

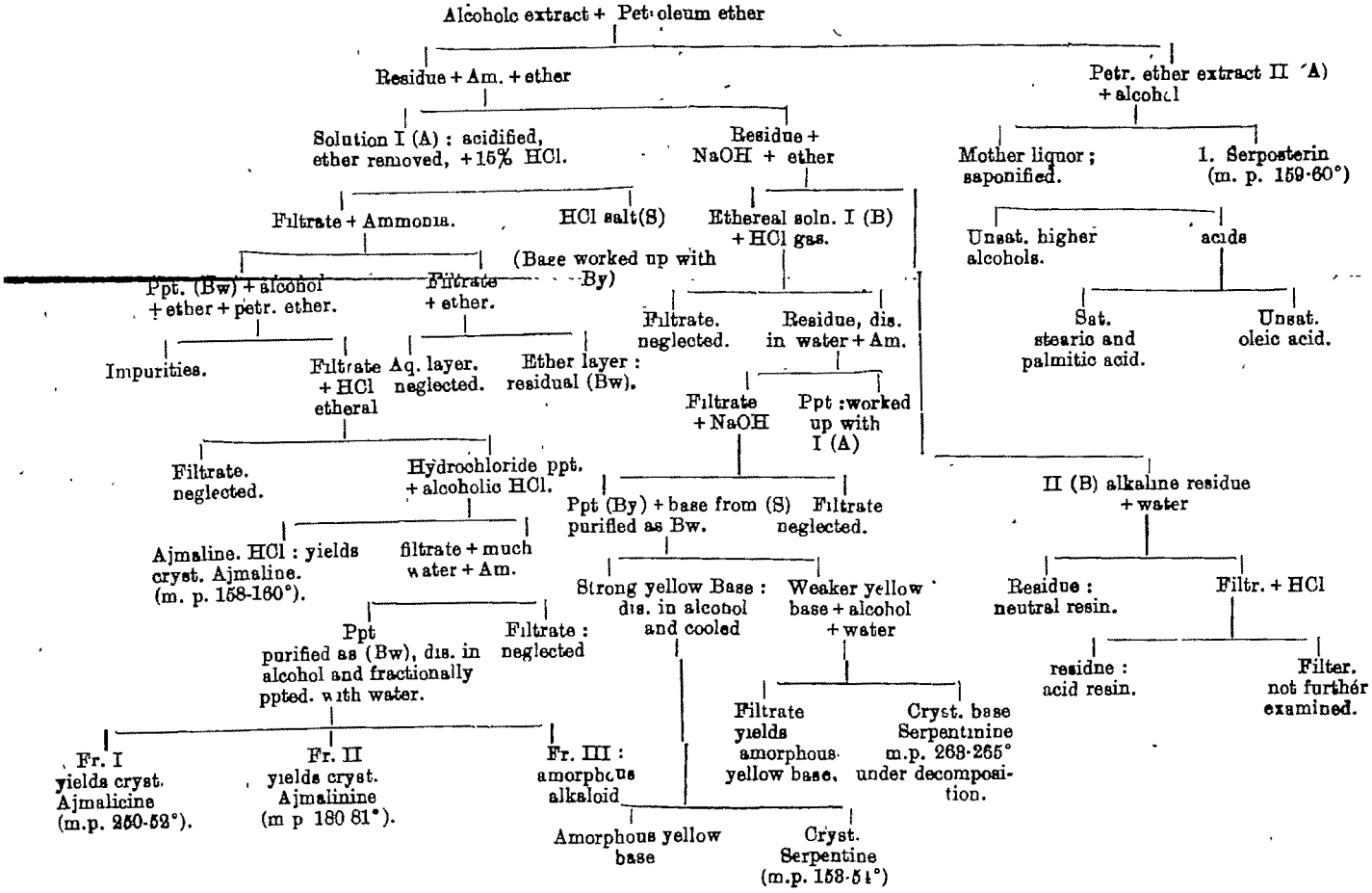
TABLE I

Colour Reactions of the Alkaloids of Rauwolfia Serpentina.

Reagent.	Ajmaline.	Ajmalinine.	Ajmalicine.	Serpentine.	Serpentinine.
Conc. H_2SO_4	Colourless	Yellow	Yellow	Yellow with greenish fluorescence	Light yellow
Conc. H_2SO_4 + $K_2Cr_2O_7$	Green	Dark brown	Dirty violet	Reddish brown	Greenish brown
Conc. H_2SO_4 + $KClO_3$	Bright yellow, then deep orange	Yellow, then dirty orange red	Deep yellow	Red	Bright yellow
Conc. H_2SO_4 + MnO_2	Violet fluorescence, then rose violet, finally orange red	Violet, then green, dirty green, finally dirty yellowish-green	Bluish-violet passing on to dirty green and finally dirty yellowish-green	Yellow, yellowish-green, dirty yellowish-brown	Dirty blue, then dirty greenish blue
Conc. HNO_3	Blood red	Yellow	Yellow	Deep yellow	Deep yellow
Frõhde's reagent	Light violet with a reddish tinge, then red	Light blue, then indigo, bluish-green, dirty green and finally grass green.	Yellowish-violet, then blue, dirty green, finally yellowish-green	Dirty yellowish-brown	Violet, then blue, greenish blue, finally dark green
Erdmann's reagent.	Rosy tinge developing into pink.	Greenish yellow, then dirty yellowish green.	Yellowish green, gradually passing on to brownish-yellow.	Light yellow, then straw coloured.	Light green then yellowish green.

TABLE II

Diagramatic scheme of Analysis of Alcoholic Extract of Roots,


Alcoholic extract + Petroleum ether
Residue + Am. + ether
Petr. ether extract II (A) + alcohol
Solution I (A) : acidified, ether removed, +15% HCl.
Residue + NaOH + ether
Mother liquor ; saponified.
1. Serposterin (m. p. 159-60°)
Filtrate + Ammonia.
HCl salt(S)
Ethereal soln. I (B) + HCl gas.
Unsat. higher alcohols.
acids
(Base worked up with By)
Ppt. (Bw) + alcohol + ether + petr. ether.
Filtrate + ether.
Filtrate. neglected.
Residue, dis. in water + Am.
Sat. stearic and palmitic acid.
Unsat. oleic acid.
Impurities.
Filtrate + HCl etheral
Aq. layer. neglected.
Ether layer : residual (Bw).
Filtrate + NaOH
Ppt :worked up with I (A)
Filtrate. neglected.
Hydrochloride ppt. + alcoholic HCl.
Ppt (By) + base from (S) purified as Bw.
Filtrate neglected.
II (B) alkaline residue + water
Ajmaline. HCl : yields cryst. Ajmaline. (m. p. 158-160°).
filtrate + much water + Am.
Strong yellow Base : dis. in alcohol and cooled
Weaker yellow base + alcohol + water
Residue : neutral resin.
Filtr. + HCl
Ppt purified as (Bw), dis. in alcohol and fractionally ppted. with water.
Filtrate : neglected
residne : acid resin.
Filter. not further examined.
Filtrate yields amorphous yellow base.
Cryst. base Serpentinine m.p. 263-265° under decomposition.
Fr. I yields cryst. Ajmalicine (m.p. 250-52°).
Fr. II yields cryst. Ajmalinine (m p 180 81°).
Fr. III : amorphous alkaloid
Amorphous yellow base
Cryst. Serpentine (m.p. 158-54°)

In conclusion the authors desire to express their indebtedness to the Trustees of the Estate of Dawoodbhoy Fazelbhoy Deceased, Bombay, for a scholarship which enabled one of them (R.H.S.) to participate in the investigations.

RESEARCH INSTITUTE,
A. V. & U. TIBBI COLLEGE, DELHI.

Received July 10, 1930

Condensation of Ethyl Propylacetoacetate with Aromatic Amines. Part I.

By G. V. Jadhav.

Although the condensation of ethyl (or methyl) acetoacetate with various aromatic amines has been worked out, chiefly by Knorr (*Ber.*, 1883, **16**, 2593; 1884, **17**, 542), Conrad and Limpach (*Ber.*, 1888, **21**, 521, 1654), Ewins and King (*J. Chem. Soc.*, 1913, **103**, 106), no systematic work has been done to observe the effect of substitution of the methylene hydrogen atoms on such condensations. Knorr (*Annalen*, 1889, **245**, 358) obtained methyl acetoacetanilide from ethyl methylacetoacetate and aniline, while Kermack and Smith (*J. Chem. Soc.*, 1931, p. 221) reported the formation of a compound $C_{21}H_{28}O_2N_4$ as a result of the interaction of *p*-anisidine and ethyl methylacetoacetate. Foglino (*Ann. Chem. Pharm.*, 1898, **26**, 535) on the other hand obtained substituted carbamides from *p*-phenetidine and various substituted ethyl acetoacetates. Guareschi (*Chem. Zentr.*, 1905, **11**, 685) describes *n*-propylacetoacetamide.

The present work was undertaken to examine the effect of substitution of the methylene hydrogen atom and also to prepare substituted quinoline derivatives. It has been found that the interaction of ethyl *n*-propylacetoacetate and aromatic amines (*viz.*, aniline, *o*-, *m*- and *p*-toluidines, *o*- and *p*-anisidines, *m*-xylidines (1:4:5 and 1:3:4) and *p*-phenetidine leads to the formation of the corresponding anilide, $MeCO{\cdot}CH{\cdot}C_3H_7{\cdot}CONHR$ or the substituted carbamide $CO(NHR)_2$ or both. The carbamide invariably is formed and its yield increases with the duration of heating. This can be explained according to Hurst and Thrope (*J. Chem. Soc.*, 1915, **107**, 934) as follows:

$$CH_3CO{\cdot}CH{\cdot}C_3H_7{\cdot}CO_2Et + PhNH_2 \longrightarrow CH_3C(=NPh){\cdot}CHC_3H_7{\cdot}CO_2Et + H_2O$$

$$\longrightarrow CH_3{\cdot}CO{\cdot}CH{\cdot}C_3H_7{\cdot}CO\ NHPh + EtOH + PhNH_2$$

$$\rightleftharpoons CO(NHPh)_2 + CH_3CO{\cdot}CH_2{\cdot}C_3H_7.$$

The carbamides are also formed on boiling the anilides with an excess of the appropriate amines.

The constitution of the carbamides was confirmed by preparing them according to Mistry and Guha (*J. Indian Chem. Soc.*, 1930, **7**, 793) and finding their mixed melting point.

In the case of carbamide it was further confirmed by boiling it with acetic anhydride and fused sodium acetate when acetanilide was obtained.

Experimental.

Diphenyl Carbamide.—The mixture of ethyl *n*-propylacetoacetate (10 g.) and aniline (5 g.) was refluxed with an air condenser for about an hour. The red liquid was then put on a water-bath to remove the alcohol formed in the reaction. The crystalline solid obtained on cooling was triturated and washed with benzene, till it was free from the unaltered substances. It was crystallised from acetic acid, m.p. 235-36°. (Found: N, 13·18. $C_{13}H_{12}ON_2$ requires N, 13·21 per cent.).

The substance was also prepared according to Mistry and Guha (*loc. cit.*) and the mixed m. p. was found to be identical.

Some of the diphenyl carbamide obtained from ethyl *n*-propylacetoacetate was boiled with acetic anhydride and anhydrous sodium acetate and when the reaction mixture was diluted, a solid was obtained having m.p. 113-14°. It was proved to be acetanilide by mixed melting point.

n-Propylacetoacetanilide—The benzene filtrate from the above preparation was evaporated to dryness and the solid obtained was drained at the pump and dried on a porous plate, as it was found easily soluble in most organic solvents, *viz.*, alcohol, chloroform, petroleum ether, methyl alcohol etc. It was finally crystallised from dilute acetic acid (1:1), m.p. 96-97°. (Found: N, 6·08. $C_{13}H_{17}O_2N$ requires N, 6·39 per cent.).

The same procedure was followed in subsequent preparations, the ester and the respective amines being taken in molecular proportions. Carbamide derivatives were found to be insoluble in benzene, the anilides being soluble. The constitution of carbamide derivatives in the case of *p*-anisidine, *o*-anisidine *m*-xylidine (1:3:4) and (1:4:5) and *p*-phenetidine was determined by preparing the compounds according to Mistry and Guha (*loc. cit.*) and by observing the mixed melting points which were found identical.

Di-o-tolyl Carbamide.—The heating was done for only half an hour and the solid was crystallised from dilute acetic acid, m.p. 246-47°. (Found: N, 11·26. $C_{15}H_{16}ON_2$ requires, N, 11·67 per cent.).

n-Propylacetoacet-o-toluidide.—The solid obtained from benzene filtrate was crystallised from dilute acetic acid, m.p. 105-106°. (Found: N, 6·30. $C_{14}H_{19}O_2N$ requires N, 6·0 per cent.).

Di-p-tolyl carbamide was prepared and purified as in the above case, m.p. 262-63°. (Found: N, 11·29. $C_{15}H_{16}ON_2$ requires N, 11·67 per cent.).

n-Propylacetoacet-p-toluidide was crystallised from dilute acetic acid, m.p. 112-13°. (Found: N, 6·2. $C_{14}H_{19}O_2N$ requires N, 6·0 per cent.).

Di-m-tolyl carbamide was crystallised from alcohol, m.p. 220°. Cossack (*Ber.*, 1879, **12**, 1449) gave 217° while Gattermann and Cantzler (*Ber*, 1892, **25**, 1089) gave 203°. Found: N, 11·35. $C_{15}H_{16}ON_2$ requires N, 11·67 per cent.).

Di-p-anisidyl Carbamide.—The heating was done for an hour and the product was crystallised from glacial acetic acid, m.p. 232-33°. Lossen (*Annalen*, 1875 **175**, 295) recorded m.p. 232-34°. (Found: N, 10·31. $C_{15}H_{16}O_3N_2$ requires N, 10·29 per cent.).

n-Propylacetoacet-p-anisidide—The solid from benzene filtrate was washed with petroleum ether and crystallised from dilute acetic acid, m.p. 115°. (Found: N, 5·44. $C_{14}H_{19}O_3N$ requires N, 5·62 per cent.).

Di-o-anisidyl Carbamide.—After heating the mixture as above, it was left at room temperature for four days, when crystals began to appear. It was then put inside a refrigerator for about twenty four hours for complete crystallisation after washing as usual, it was finally crystallised from dilute acetic acid, m.p. 185-86°. Conard and Limpach (*loc. cit.*) gave m.p. 182°. Mühlhaüser (*Annalen*, 1881 **207**, 244) gave 174°. (Found: N, 9·72. $C_{15}H_{16}O_3N_2$ requires N, 10·29 per cent.).

Di-m-xylidyl Carbamide (1:3:4).—Heating was done for only twenty minutes. It was crystallised from glacial acetic acid, m.p. 239-40°. (Found: N, 10·62. $C_{17}H_{20}ON_2$ requires N, 10·45 per cent.).

n-Propylacetoacet-m-xylidide (1:3:4).—The solid was first washed with petroleum ether and finally crystallised from dilute

alcohol, m.p. 100-101°, (Found: N, 5·92. $C_{15}H_{21}O_2N$ requires N, 5·66 per cent.).

Di-m-*xylidyl carbamide* (1:4:5) was prepared and crystallised as in the case of (1:3:4), m.p. above 275°. (Found: N, 10·17. $C_{17}H_{20}ON_2$ requires N, 10·45 per cent.).

n-Propylacetoacet-m-*xylidide* (1:4:5) was washed as in the case of (1:3:4), m.p. 113-14°. (Found: N, 5·86. $C_{15}H_{21}O_2N$ requires N, 5·67 per cent.).

Di-p-*phenetidyl Carbamide*.—The mixture was heated for an hour. The solid was crystallised from glacial acetic acid, m.p. 226°, (Foglino, *loc. cit.*). (Found: N, 9·66. $C_{17}H_{20}O_3N_2$ requires N, 9·33 per cent.).

n-Propylacetoacet-p-*phenetidide*.—It was washed with petroleum ether and finally crystallised from dilute acetic acid, m.p. 115°. (Found: N, 5·57. $C_{15}H_{21}O_3N$ requires N, 5·32 per cent.).

Chemical Laboratories,
Royal Institute of Science, Bombay.

Received July 8, 1931.

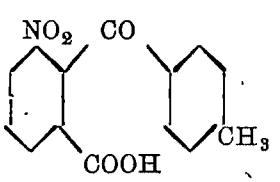
Studies in the Anthraquinone Series. Condensation of 3 : 5-Dinitrophthalic Acid with Toluene.

By Profulla Chandra Mitter and Rashbehari Goswami.

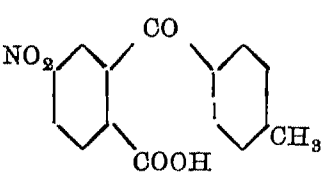
The hydroxyanthraquinones are abundant in nature usually in the form of glucosides, from which important compounds like alizarin, purpurin, etc., are obtained. On account of the valuable tinctorial and medicinal properties exhibited by many of these, the study of their composition and synthesis has long been a subject of considerable interest.

The condensation of nitrophthalic anhydrides with phenols and hydrocarbons and the subsequent conversion of the resulting nitrobenzoylbenzoic acids into hydroxyanthraquinones is one of the various methods available for the synthesis of these substances. The position of the hydroxyl-groups in the resulting anthraquinone can be ascertained from a knowledge of the position of the nitro-groups in the phthalic anhydride molecule and the manner in which the nitrophthalic anhydrides condense with the reacting substances. So, it would be of interest to study the influence of nitro-groups on the condensation of nitrophthalic anhydrides with other bodies.

Mitter and Sarkar (*J. Indian Chem. Soc.*, 1930,7, 619,) found that 3-and 4-nitrophthalic anhydrides condense with toluene to give the compounds (I) and (II) respectively.



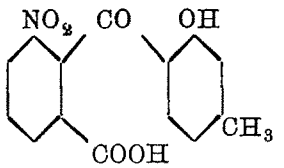
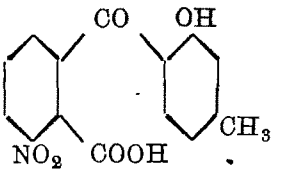
(I)



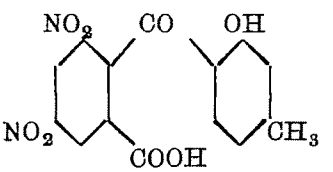
(II)

It would appear from these observations that of the two carboxyl groups, the one nearer to a nitro-group is more reactive than the other.

Eder and Widmer (*Helv. Chim. Acta*, 1922, **5**, 3) found that with 3-nitrophthalic acid and *m*-cresol two nitrobenzoylbenzoic acids are obtained.

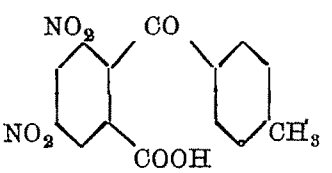



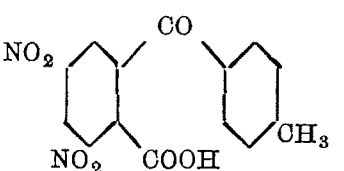
So the nature of the substance reacting has also some influence on the nature of the product formed. The same authors (*Helv. Chim. Acta*, 1923, **6**, 966) condensed *m*-cresol with 3 : 5-dinitrophthalic anhydride and here they obtained only one product, *viz.*,



in the formation of which the contiguity of the nitro-group to the carboxyl group was probably the determining factor.

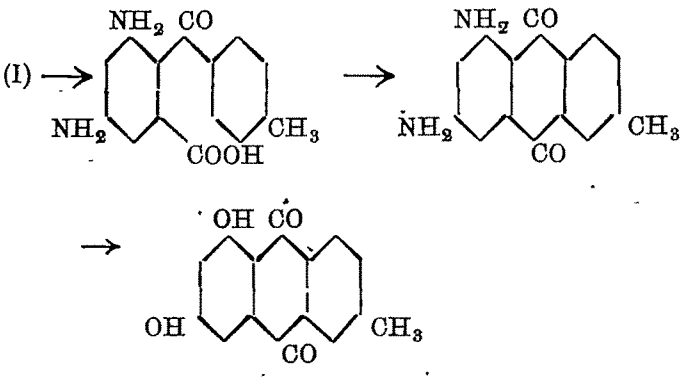
When 3 : 5-dinitrophthalic anhydride is condensed with toluene in presence of aluminiun chloride only one product is obtained which may have either of the two formulae.


(III)


(IV)

After reducing the nitro-groups a diamino-acid is obtained which is converted into a diaminoanthraquinone by the action of sulphuric acid. On diazotisation a dihydroxyanthraquinone is obtained which is identical with the dihydroxymethylanthraquinone obtained by the condensation of 3 : 5-dihydroxybenzoic acid with *p*-toluic acid (Marchlewski, *J. Chem. Soc.*, 1893, **63**, 1137). The condensation product of 3 : 5-dinitrophthalic anhydride with toluene has therefore the formula (III), the anhydride behaving with toluene in the same way as

with *m*-cresol. The contiguity of a nitro-group is here the determining factor in the reactivity of a carboxyl group.



EXPERIMENTAL.

3:5-*Dinitrophthalic Anhydride*.—3: 5-Dinitro-*o*-toluic acid (5 g.) prepared by the method of Jacobsen and Wierss (*Ber.*, 1883, **16**, 1956) was oxidised according to the method of Racine (*Annalen*, 1887, **239**, 71) by heating in a sealed tube with dilute nitric acid (25 c.c., *d* 1·15) to 170° for six hours instead of at 160° for five hours as suggested by the author. The slight modification is found to improve the yield.

The well-dried acid is refluxed with five times its weight of acetic anhydride for about an hour. The excess of acetic anhydride is distilled off at a reduced pressure. The residue is recrystallised from benzene, m.p. 162-64°.

3:5-*Dinitro*-2-*p*-*toluoylbenzoic Acid*.—3:5-Dinitrophthalic anhydride (5 g.) is suspended in toluene (75 c.c.) and powdered anhydrous aluminium chloride (20 g.) gradually added to the mixture with constant shaking, in about two hours. The reaction takes place at the ordinary temperature. The excess of toluene is distilled off in steam, the crude acid boiled with calcium carbonate, filtered and acidified. It is recrystallised from glacial acetic acid in yellow plates, m.p. 237°. (Found: C, 54·53 ; H, 3·35 ; N, 8·53 ; M. W. (by titration), 330. $C_{15}H_{10}O_7N_2$ requires C, 54·54; H, 3·03; N, 8·48 per cent., M. W. 330).

3:5-*Diamino*-2-*p*-*toluoylbenzoic Acid*.—To a solution of ferrous sulphate (70 g.) in 60 c.c. of water, heated to boiling, liquor ammonia (120 c.c.) is added and then an ammoniacal solution of 3:5-dinitro-2-*p*-toluoylbenzoic acid is slowly poured in, the mixture being

well-shaken all the time. When the reaction is complete, the mixture is heated to boiling for about fifteen minutes and filtered. The residue is repeatedly extracted with boiling water and the combined filtrates evaporated to a small volume on the water-bath. This is filtered and after digesting with animal charcoal the filtrate is acidified with dilute acetic acid when a semi-solid precipitate is obtained which solidifies on drying on a porous plate. Yellow needles from water, m.p. 170-71°. (Found: N, 10·55; M. W., 269. $C_{15}H_{14}O_3N_2$ requires N, 10·37 per cent., M. W., 270).

1:3-*Diamino-6-methylanthraquinone.*—The diamino- acid obtained in the previous operation (1 g.) is added to strong sulphuric acid (*d* 1·84) heated to 160° in an oil-bath and kept at 160-70° for twenty minutes. On pouring on ice a red mass separates which is extracted with dilute soda solution. The residue crystallises from pyridine in fine red needles, m.p. 265°. (Found: N, 11·45. $C_{15}H_{12}O_2N_2$ requires N, 11·11 per cent.).

1:3-*Dihydroxy-6-methylanthraquinone.*—Diaminoanthraquinone (0·5 g.) was dissolved in strong sulphuric acid (5 g.) and the calculated amount of powdered sodium nitrite was added with constant stirring under ice-cooling until an excess of nitrous acid was detected by starch-iodide paper. The mixture was then heated on the water-bath for an hour and then poured on ice. The precipitate was filtered, washed, dried on a porous plate and extracted with benzene. On recrystallisation from the same solvent, the melting point was found to be 267° which was not altered on mixing with an equal amount of 1:3-dihydroxy-6-methylanthraquinone obtained by condensing 3:5-dihydroxybenzoic acid with *p*-toluic acid. Hence it was concluded that the two substances must be identical. The quantity of the substance was not sufficient for an analysis.

University College of Science and Technology, Calcutta

Received July 25, 1931.

Studies on the Reaction of Silver Nitrate with Organic Sulphides.

By Prafulla Chandra Rây, Nadiabehari Adhikari and Harendranath Rây.

The interaction of organic sulphides on gold chloride has been systematically studied and compounds of the type $AuCl_3 \cdot R_2S$ and $AuCl \cdot R_2S$ (where R is an alkyl radicle) have been obtained (Phillips, *J. Amer. Chem. Soc.*, 1901, 23, 257; Rây and Sen, *J. Indian Chem. Soc.*, 1930, 7, 67). From the fact that silver occurs with gold in the same group of the periodic table, it was expected that salts of silver might also interact with organic sulphides giving rise to compounds similar to those of monovalent gold. In fact, compounds of the types $AgNO_3 \cdot R_2S$ and $AgNO_3 \cdot R_2S_2$ have actually been obtained as a result of the interaction of alkyl sulphides and disulphides with silver nitrate. A compound of the formula $3AgNO_3 \cdot 2(C_3H_5)_2S$ has also been obtained as a result of the interaction of allyl sulphide with silver nitrate. By the action of mercuric chloride on the above silver salts, some interesting mercury compounds have also been obtained.

The following compounds have been prepared as a result of these reactions:

1. $AgNO_3 \cdot (CH_3)_2S$.
2. $AgNO_3 \cdot (C_2H_5)_2S$.
3. $AgNO_3 \cdot (C_3H_7)_2S$.
4. $AgNO_3 \cdot (C_4H_9)_2S$.
5. $AgNO_3 \cdot (C_7H_7)_2S$.
6. $AgNO_3 \cdot (CH_3)_2S_2$.
7. $AgNO_3 \cdot (C_2H_5)_2S_2$.
8. $AgNO_3 \cdot (C_7H_7)_2S_2$.
9. $AgNO_3 \cdot S\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}$.
10. $3AgNO_3 \cdot 2(C_3H_5)_2S$.
11. $Hg(NO_3)_2 \cdot 2(CH_3)_2S$.
12. $HgCl(NO_3) \cdot (C_2H_5)_2S$.
13. $HgCl(NO_3) \cdot (C_4H_9)_2S$.

These silver compounds were found to be binary electrolytes from their conductivity data. The silver ion can be precipitated as silver chloride from the solution of the salts by means of hydrochloric acid. With potassium ferrocyanide and potassium chromate they give the respective silver compounds as with silver nitrate. These reactions

show that these compounds are either imperfect complexes or molecular compounds, the alkyl sulphide groups being loosely attached to the silver nitrate molecule. This is also confirmed from the interaction of the bases like ammonia and pyridine upon these silver salts, when the loosely attached alkyl sulphide molecules are replaced by the bases. The mercury compounds are most probably formed as follows:

1. $2\,AgNO_3\cdot(CH_3)_2S + HgCl_2 = 2\,AgCl + 2(CH_3)_2S + Hg(NO_3)_2$.
   $Hg(NO_3)_2 + 2(CH_3)_2S = Hg(NO_3)_2\cdot 2(CH_3)_2S$.
2. $AgNO_3\cdot(C_2H_5)_2S + HgCl_2 = HgClNO_3\cdot(C_2H_5)_2S + AgCl$.

It will be found that one molecule of a mono- or a disulphide combines with one molecule of silver nitrate. But in the case of allyl sulphide, which is the only unsaturated sulphide dealt with, two molecules combine with three molecules of silver nitrate. The monosulphide compounds of silver have definite melting points but disulphide compounds decompose on melting. The melting points of the compounds as well as the solubilities in water and alcohol show a marked gradation of properties. The former diminish as we pass from methyl to butyl sulphide. The solubility of the salts in water decreases as we ascend the series and the same thing takes place in alcohol as we descend the series, *i.e.*, from butyl to methyl sulphide. The compounds are very unstable. They decompose when exposed to light and moisture. The decomposition of the disulphide compounds is very rapid.

The mercury compounds are white crystals with definite melting points. They are soluble in many organic solvents as well as in water and can be crystallised from cold alcohol.

Experimental.

Preparation of $AgNO_3\cdot(CH_3)_2S$.—Methyl sulphide was added to a concentrated solution of silver nitrate. After some time crystals of the compound separated out. It was crystallised from alcohol, m.p. 126°. (Found: Ag, 46·71; NO_3, 26·08; C, 10.34. $AgNO_3\cdot(CH_3)_2S$ requires Ag, 46·55; NO_3, 26·72; C, 10·34 per cent.).

Preparation of $AgNO_3\cdot 2\,C_5H_5N$ (Jörgensen, *J. pr. Chem.*, 1886, *ii*, **33**, 501). Nearly 2 g. of the substance $AgNO_3\cdot(CH_3)_2S$ were dissolved in 6—8 c.c. of pyridine, filtered and treated with ether. While stirring, crystals of $AgNO_3\cdot 2C_5H_5N$ separated out. (Found:

Ag, 32·60; N, 12·80. $AgNO_3 \cdot 2C_5H_5N$ requires Ag, 32·92; N, 12·80 per cent.).

Preparation of $AgNO_3 \cdot (C_2H_5)_2S$.—As above, to a concentrated solution of silver nitrate, ethyl sulphide was added drop by drop. The liquid was stirred, crystals separated out with evolution of heat and were recrystallised from alcohol, m.p. 112°. (Found: Ag, 41·91; NO_3, 28·42; C, 18·89. $AgNO_3 \cdot (C_2H_5)_2S$ requires Ag, 41·53; NO_3, 23·84; C, 18·5 per cent.). Molar conductivity at infinite dilution in water was found to be 116 r.o.

Preparation of $AgNO_3 \cdot (C_3H_7)_2S$.—Propyl sulphide was added to a solution of silver nitrate. It was cooled and stirred, crystals separated out and was recrystallised from alcohol, m.p. 109°. (Found: Ag, 37·35; NO_3, 21·51; C, 24·737. $AgNO_3 \cdot (C_3H_7)_2S$ requires Ag, 37·50; NO_3, 21·53; C, 25·00 per cent.).

Preparation of $AgNO_3 \cdot (C_4H_9)_2S$.—This compound can be prepared as before by adding butyl sulphide to a solution of silver nitrate. The substance was also crystallised from alcohol, m.p. 98°. (Found: Ag, 34·36; NO_3, 19·25; C, 30·01. $AgNO_3 \cdot (C_4H_9)_2S$ requires Ag, 34·17; NO_3, 19·62; C, 30·88 per cent.).

Silver nitrate ammonia, $AgNO_3 \cdot 2NH_3$; (Wetzlar, "Hofmann's Lexicon", Vol. I .(*i*), p. 906). About 1—2 g. of the compound $AgNO_3 \cdot (C_4H_9)_2S$ were treated with freshly prepared alcoholic ammonia. The mixture was warmed for some time and allowed to cool. Crystals of $AgNO_3 \cdot 2\ NH_3$ separated out. It was washed with alcohol and dried. (Found: Ag, 52·25; N, 19·81. $AgNO_3 \cdot 2NH_3$ requires Ag, 52·94; N, 20·58 per cent.).

Preparation of $AgNO_3 \cdot (C_7H_7)_2S$.—An alcoholic solution of the sulphide was added to an aqueous solution of silver nitrate. The compound $AgNO_3 \cdot (C_7H_7)_2S$ together with benzyl sulphide separated. The mixture was fractionally crystallised from alcohol two or three times and washed several times with ether in which benzyl sulphide is highly soluble and $AgNO_3 \cdot (C_7H_7)_2S$ is only moderately soluble, m.p. 93—95°. (Found: Ag, 28·02; NO_3, 15·28; C, 43·44. $AgNO_3 \cdot (C_7H_7)_2S$ requires Ag, 28·12; NO_3, 16·14; C, 43·76 per cent.).

Preparation of $AgNO_3 \cdot (CH_3)_2S_2$.—As we pass from mono- to disulphide the reaction takes a violent form. Reactions of this kind must be carried out at a low temperature. The silver nitrate solution was cooled in a freezing mixture for some time and the disulphide was added gradually. The crystals formed were filtered

and recrystallised from alcohol at 0°. It decomposes explosively. (Found: Ag, 40·72; NO_3, 23·14; C, 8·97. $AgNO_3 \cdot (CH_3)_2S_2$ requires Ag, 40·91; NO_3, 23·43; C, 9·09 per cent.).

Preparation of $AgNO_3.(C_2H_5)_2S_2$.—This compound was prepared by the above process. (Found: Ag, 37·32; C, 16·16. $AgNO_3 \cdot (C_2H_5)_2S_2$ requires Ag, 36·98; C, 16·44 per cent.).

Preparation of $AgNO_3 \cdot (C_7H_7)_2S_2$.—An alcoholic solution of dibenzyldisulphide was added to a concentrated solution of silver nitrate. Mixtures of $AgNO_3 \cdot (C_7H_7)_2S_2$ and the disulphide were formed. The latter being soluble in alcohol was removed and the former was crystallised out,. m.p. 103°. (Found: Ag, 25·57; C, 44·05. $AgNO_3 \cdot (C_7H_7)_2S_2$ requires Ag, 25·95; C, 40·38 per cent.)

Preparation of $AgNO_3 \cdot (CH_3 \cdot C_2H_5)S$.—This reaction was started by the action of the sulphide upon finely powdered silver nitrate. The mixture was stirred intimately. It was placed in the dark overnight. The mass swelled up and was crystallised from alcohol. (Found: Ag, 44·25; C, 14·35. $AgNO_3 \cdot (CH_3 \cdot C_2H_5)S$ requires Ag, 43·90; C, 14·63 per cent.).

Preparation of $3\ AgNO_3 \cdot 2(C_3H_5)_2S$.—To a cooled concentrated solution of silver nitrate the sulphide was added gradually and stirred. The crystals separated out. It is slightly soluble in alcohol, m. p. 152°. (Found: Ag, 44·29; C, 19·36; S, 8·32. $3AgNO_3 \cdot 2(C_3H_5)_2S$ requires Ag, 43·90; C, 19·51; S, 8·67 per cent.).

Preparation of $Hg(NO_3)_2 \cdot 2(CH_3)_2S$.—$AgNO_3 \cdot (CH_3)_2S$ was dissolved in alcohol. To this solution, calculated amount of mercuric chloride in alcohol was added. Silver chloride separated out. It was allowed to settle and filtered. To the filtrate ether was added when the above mentioned compound precipitated out. (Found: Hg, 44·14; N, 6·0; C, 10·39. $Hg(NO_3)_2 \cdot 2(CH_3)_2S$ requires Hg, 44·64; N, 6·25; C, 10·71 per cent.).

Preparation of $HgClNO_3 \cdot (C_2H_5)_2S$, $HgClNO_3 \cdot (C_3H_7)_2S$ *and* $HgClNO_3 \cdot (C_4H_9)_2S$.—To the alcoholic solutions of $AgNO_3 \cdot (C_2H_5)_2S$, $AgNO_3 \cdot (C_3H_7)_2S$ and $AgNO_3 \cdot (C_4H_9)_2S$, excess of mercuric chloride in alcohol was added separately. In each case silver chloride together with a white compouud separated out. To the filtrate ether was added and the compound that separated out was filtered and dried. The silver chloride admixture was warmed with alcohol and filtered. The filtrate deposited beautiful crystals. The melting points of

the two fractions *viz.*, (1) obtained from ether and (2) obtained from alcohol were identical. $HgClNO_3 \cdot (C_2H_5)_2S$ melts at 110°. (Found: Hg, 51·54 ; C, 12·29 ; Cl, 9·16. $HgClNO_3 \cdot (C_2H_5)_2S$ requires Hg, 51·61 ; C, 12·39 ; Cl, 9·16 per cent.).

The conductivity of the compound $HgCl(NO_3) \cdot (C_2H_5)_2S$ was determined by dissolving 0·7896 g. of the substance in 100 c.c. of water at 31°. The solution was then successively diluted twice, thrice and four times and the conductivity of each determined. 1, 2, 3, 4 respectively represent these solutions.

Solution.	Molar conductivity r.o.	Conc. of electrolyte mole/litre.
1	83·08	·0203
2	88·16	·00507
3	97·52	·00253
4	122·92	·00127

The compound $HgClNO_3 \cdot (C_3H_7)_2S$ melts at 100-102°. (Found: Hg, 48·008; Cl, 8·32. $HgClNO_3 \cdot (C_3H_7)_2S$ requires Hg, 48·13 ; Cl, 8·54 per cent.).

The compound $HgClNO_3 \cdot (C_4H_9)_2S$ melts at 132°. (Found: Hg, 44·73 ; Cl, 7·99. $HgClNO_3 \cdot (C_4H_9)_2S$ requires Hg, 45·09 ; Cl, 8·004 per cent.).

The reaction of *iso*butyl and *iso*amyl sulphides on silver nitrate was also tried. In the latter case, a thick syrupy liquid was obtained with perceptible evolution of heat. With the former, nothing remarkable happened and the sulphide separated out as an oil. Reaction with phenyl sulphide produced a clay-like amorphous substance.

PALIT PROFESSOR'S LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
CALCUTTA.

Received April 1, 1931.

A Method for the Determination of Titanium as Phosphate.

By J. C. Ghosh.

For the determination of small quantities of titanium, the colorimetric method is very satisfactory, except when vanadium, chromium or alkali salts are present. The Gooch method (*Chem. News*, 1885, **52**, 55, 68) depends upon adding alkali acetate and carrying out a basic acetate precipitation. The Baskerville method (*J. Amer. Chem. Soc.*, 1894, **16**, 427, 475; Gooch, *Proc. Amer. Acad. Arts Sci.*, 1885, **12**, 435; Chatard, *Amer. Chem. J.*, 1891, **13**, 106) is based upon the fact that a nearly neutral solution of iron and titanium chlorides when boiled with sulphurous acid at moderate dilution gives a precipitate of titanium hydroxide, while the iron remains in solution in the ferrous state. Thornton (*Amer. J. Sci.*, 1914, *iv*, **37**, 173, 407) recommends the use of cupferron. The Chancel-Stromayer method consists of precipitating titanium with sodium thiosulphate added to the pyrosulphate melt. The method of Barneby and Isham (*J. Amer. Chem. Soc.*, 1910, **32**, 957) consists of fusion with sodium carbonate and a little potassium nitrate, extraction with hot water, solution of the ferric oxide and sodium titanate in HCl, extraction of the ferric chloride with ether, reduction of the slight traces of iron with sulphurous acid, precipitation of the titanic acid by boiling in acetic acid solution, filtration and ignition of the precipitate to titanium dioxide.

In presence of phosphoric acid, the precipitation of *meta*-titanic acid is hindered due to hydrolysis; so there is always a risk of precipitating it in the presence of any soluble phosphates. But if the titanium is precipitated wholly as a phosphate, it can be determined quantitatively. The method as worked out by the author is given below.

Experimental.

Any ore of titanium or titanium-bearing clay *viz.*, bauxite, is first powdered very finely and passed through a 90-mesh sieve. The sample is then dried at 110°. The dried sample is taken for analysis. From 0·5 to 1·0 g. of the sample is first fused in a platinum

crucible with sodium carbonate for at least half an hour (some ores require a preliminary treatment with HF and H_2SO_4, prior to fusion). This converts the titanium into sodium titanate. The melt is now leached with 200 c.c. of boiling water, filtered and washed thoroughly with hot water. Alumina and silica go into solution both as soluble sodium salts. The filtrate is rejected; titanium remains in the residue as sodium titanate, Na_2TiO_3. (This sodium titanate undergoes hydrolysis and an acid titanate of sodium, $2Na_2O \cdot 9TiO_2, 5H_2O$ is precipitated. Though sodium titanate is hydrolysed in water, none of it goes into solution. This is soluble, in both sulphuric and hydrochloric acids. But the HCl solution when boiled long is again hydrolysed and *meta*-titanic acid is precipitated). About 30 c.c. of dilute H_2SO_4 (1 : 5) is added to the residue and gently boiled to dissolve. The solution is then cooled a little, diluted to 200 c.c. with cold water, nearly neutralised with ammonium hydroxide and 20 c.c. of 20 p.c. solution of ammonium phosphate are added. Then the solution is further diluted with hot water to about 400 c.c. If a precipitate forms at this stage, it is just dissolved with dilute H_2SO_4 and an excess of 5 c.c. acid is further added. The amount of free H_2SO_4 in the solution should not exceed 2 per cent. Now 10 g. of sodium thiosulphate and 15 c.c. of pure acetic acid are added (this will reduce all the iron in the ferric state to the ferrous state) and the solution boiled for about half an hour. Now all the titanium will be precipitated as phosphate, leaving iron in solution. (When solutions containing iron entirely in the ferrous state are treated with an alkali phosphate in presence of excess of $Na_2S_2O_3$, no iron is precipitated). The solution is now filtered and the residue is washed well with hot water, ignited and weighed as $Ti_2P_2O_9$.

The reactions are as follows :—

Titanium forms a basic phosphate with acid or a soluble phosphate.

$$TiO_2 \cdot H_3PO_4 \rightarrow TiO_2 \cdot HPO_3, H_2O.$$

or, $2TiO_2 \cdot HPO_3, 2H_2O \rightarrow 2TiO_2 \cdot P_2O_5, 3H_2O.$

In presence of sulphuric acid it will give

$$2TiO(SO_4) + 2H_3PO_4 \rightarrow 2TiO_2 \cdot 2HPO_3 + 2H_2SO_4.$$

This residue when ignited leaves a pyrophosphate of the composition; $2TiO_2 \cdot P_2O_5$ or $Ti_2P_2O_9$.

$$Ti_2P_2O_9 \times 0{\cdot}63 = TiO_2.$$

Some experimental data are given below. Pure TiO_2 of known composition was taken for analysis.

TABLE I.

Wt. of phosphate.	Wt. of TiO_2 from phosphate.	Wt. of TiO_2 detmd. as oxide.	Actual wt. of TiO_2 taken.
0·2760 g.	0·1463 g.	0·1442 g.	0·1450 g.
0·2270	0·1203	0·1206	0·1210
0·2830	0·1500	0·1520	0·1520
0·1770	0·0938	0·0948	0·0945
0·1764	0·0935	0·0944	0·0945

All the above results were obtained by using H_2SO_4 as the solvent for the leached residue.

By using dilute hydrochloric acid as the solvent, the following results were obtained.

TABLE II.

Wt. of phosphate.	Wt. of TiO_2 from phosphate.	Wt. of TiO_2 detmd. as oxide.	Actual wt. of TiO_2 taken.
0·1710 g.	0·0906 g.	0·0930 g.	0·0910 g.
0·2951	0·1564	0·1580	0·1565

From the above figures it is evident that it does not matter much if H_2SO_4 or HCl is used as the solvent for the leached residue.

In the case of natural ores the following figures were obtained.

TABLE III.

Wt. of phosphate-precipitate.	Wt. of TiO_2 from phosphate.	TiO_2 determined by Oxide-method.
A. 0·3755 g.	0·1990 g.	0·1988 g.
0·3752	0·1988	0·1984
B. 0·3775	0·2001	0·2000
0·3779	0·2003	0·2001
C. 0·1899	0·1006	0·1006
0·1900	0·1007	0·1006

The sample 'A' contained 54·88 p.c. iron; sample 'B' contained 40·44 p.c. iron and sample 'C' contained 56·80 p.c. iron.

Analysis of samples of Ilmenite.—0·5 G. of the sample was taken for analysis.

TABLE IV.

Wt. of phosphate-precipitate.	Wt. of TiO_2 from phosphate.	TiO_2 determined by Oxide-method
0 4566 g.	0·2420 g.	0·2420 g.
0·4575	0·2425	0 2429
0·4585	0 2430	0·2411

Analysis of a sample of Bauxite from the Central Provinces of India.—1·0 G. of the sample was taken for analysis.

TABLE V.

Wt. of phosphate-precipitate.	Wt. of TiO_2 from phosphate.	TiO_2 determined by Oxide-method.
0·2951 g.	0 1564 g.	0 1580 g.
0·2950	0 1564	0·1584

From the above experiments it is conclusively proved that titanium can be determined quantitatively as phosphate.

These precipitates of phophates did not give variable results even when fused over and over again to get constant values and the operation repeated.

This method has the advantage that Ti is separated from Fe and almost all other metals except Zr, in a form that may be easily filtered and washed and is serviceable for the determination of small quantity of Ti, in presence of Fe. [This method is inapplicable in presence of thorium also.]

CHEMICAL LABORATORY,
THE TATA IRON & STEEL CO., LTD.,
JAMSHEDPUR.

Received June 29, 1931.

Reactivity of Conjugated Systems. Part IV. Condensation of Alkylidene Ketones with Cyanoacetamide.

By Chittaranjan Barat.

In previous communications of this series (Barat, *J. Indian Chem. Soc.*, 1930, **7**, 821; 1931, **8**, 37), it has been shown that in a conjugated system of the type R·CH=CH·X, the reactivity of the ethylenic linkage towards additive reactions with regard to reactive methylene groups is governed to a considerable extent by the nature of the negative character of the group X, which consists of a so-called negative grouping containing a carbonyl group in conjugation with the ethylenic, and follows the three-carbon system rule of Lapworth and McRae (*J. Chem. Soc.*, 1922, **121**, 2747), and also of Kon and his collaborators (*ibid.*, 1923, **125**, 1361; and subsequent papers). In other words it has been fully substantiated there by keeping R constant and varying the nature of the substituent X, that the reactivity of this ethylenic bond is enhanced by an increase in the negative character of X, and *vice versa*. Thus the order of the yields or the condensation products as well as their ease of formation follow the order:

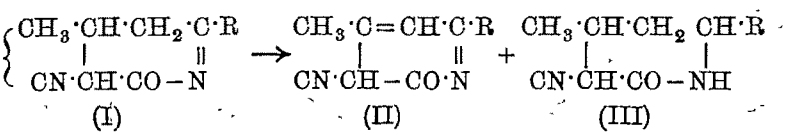
$$X=\overline{CO}\cdot C_6H_4\cdot Me > CO\cdot Ph > CO\cdot Me > CO\cdot Et > CO\cdot NH_2 > CO\cdot OEt.$$

In the present work R has been changed from the aryl group Ph into the alkyl group Me, and it has been found that the activity is appreciably enhanced, subject, however, to the nature of the substituent X. This difference might, of course be due to two causes, *viz.*, (1) the less negative nature of the methyl group than phenyl, or, (2) the smaller volume occupied by the former than the latter—thus offering less steric obstruction to the primary additive reaction, which, necessarily precedes the subsequent ring-closure by the elimination of water.

From the evidence in hand, this latter cause seems to be more reasonable, as by taking mesityl oxide, where there are two methyl

groups attached to the left hand carbon atom, the yield of the condensation product is much lower than when there is only one (in the case of ethylidene acetone), which must be due to the greater steric hindrance offered by two methyl groups than by only one.

As has already been pointed out in Part I of this series, (Barat *loc. cit.*), the tetrahydropyridine derivatives obtained from these reactions pass into the corresponding dihydropyridine compounds by dehydrogenation quite readily in presence of oxidising agents like nitrous acid or bromine and slowly by a process of reciprocal oxidation and reduction when left in an alkaline medium like alcoholic ammonia, when one molecule of the original condensation product is dehydrogenated into a dihydropyridone at the expense of another, which is, of necessity, reduced into the corresponding hexahydro-derivative. The observation of Sen (*J. Chem. Soc.*, 1915, **107**, 1366; *cf.* also Barat, *J. Indian Chem. Soc.*, 1930, **7**, 855), in obtaining a dihydropyridone from benzylidene acetone and cyanoacetamide has been a specific case of such a phenomenon on record. But whilst this reaction has been extremely slow in cases where R in the above system is Ph, it appears to be fairly rapid in the case of the present series, *i.e.*, when R is Me, as even during the ordinary course of Michael's reaction quite an appreciable quantity of the dihydropyridone (II), is obtained. This, by virtue of its sparing solubility, is easily separated from the rest of the condensation product which contains the corresponding quantity of the hexahydro-derivative (III), along with the usual condensation product (I).

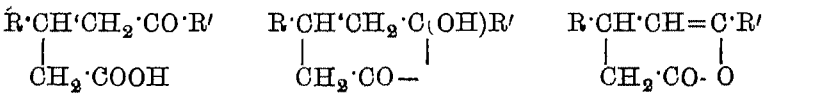


(I) (II) (III)

The remaining mass consequently exhibits an impure nature by not melting sharply even after crystallisation, by virtue of a similar solubility of the two constituents. The original product however, was finally obtained in a fairly pure condition after repeated crystallisations from alcohol, the small proportion of the hexahydro-compound remaining in the mother-liquor. On hydrolysis it gave an open-chain δ-ketonic acid analogous to those described previously (*loc. cit.*).

Quite recently a contradiction has been made by Qudrat-i-Khuda (*J. Indian Chem. Soc.*, 1931, **8**, 215), regarding the keto-lactol configuration of these δ-ketonic acids, ascribed to them in Part I of this series. He attributes an open-chain configuration to these com-

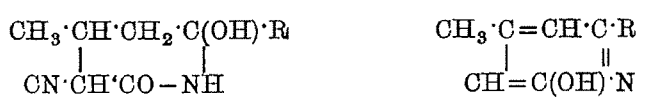
pounds which were described by the present author as closed ring keto-lactols on the ground that they are soluble in sodium bicarbonate solution, in a finely ground condition and as such must contain free carboxyl groups. On careful repetition of the previous experiments it has now been found that these substances dissolve very slowly in cold bicarbonate solution, but the rate of dissolution does not indicate a free carboxyl group at any rate; further the formation of an unsaturated lactone (VI), by treatment with acetyl chloride or acetic anhydride, strongly indicates the probability of at least a momentary existence of the lactol form (V), since the formation of (VI) cannot be explained from an open-chain ketonic structure (IV) (*cf.* Vorländer and Knotzsch, *Annalen*, 1897, **294**, 333).



(IV) (V) (VI)

It must be observed, however, that between a " fixed keto-lactol configuration" and a "no keto-lactol configuration" there may be intermediate stages (depending upon the nature and volume of substituents and other probable considerations) where some sort of a loose keto-lactol phase may exist. The existence of an equillibrium between the keto-acid and the keto-lactol is not unlikely in these cases as in many instances where an aldol form is possible it has usually been isolated. (*cf.* the case of hydroxypiperidine derivatives (VII) described herein, as well as the case of *pseudo*-urethanes, Sen and Barat, *J. Indian Chem. Soc.*, 1926, **3**, 405). It is evident nevertheless, that the constitution of these compounds cannot be fully cleared up without physico-chemical experiments. This will be taken up as soon as time and opportunity permit. Till then these compounds have been provisionally described as open-chain δ-ketonic acids.

The products obtained by Knoevenagel's reaction consist of the hydroxypiperidine derivatives (VII) which are readily converted into the Michael compounds (I) upon dehydration, and give upon hydrolysis the same δ-ketonic acids as afforded by the corresponding Michael compounds.



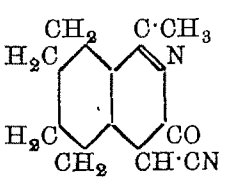
(VII) (VIII)

These tetrahydropyridones can be converted into the corresponding dihydro-derivatives by means of nitrous acid or bromine. The latter when hydrolysed by 75 p.c. sulphuric acid in the usual way give the hydroxypyridines (VIII) characterised by their colour reactions with ferric chloride.

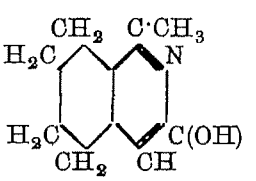
Mesityl oxide behaves differently from these ethylidene ketones by giving the hydroxypiperidine derivative (analogous to VII,) even with sodium ethoxide; such that identical compounds are obtained both by Michael's and Knoevenagel's reactions. The aldol phase, however, is easily removable when dehydrated in the usual way. The most interesting feature of this compound is its failure to give rise to a dihydro-derivative with nitrous acid or bromine, which confirms the statement made in Part I of this series that it is the 4 and 5 carbon atoms of these tetrahydropyridones that are removed during dehydrogenation, and corroborates the constitution ascribed to these bodies in that paper. This stability towards dehydrogenating agents is doubtlessly due to there being no hydrogen atom attached to the carbon atom 4, without the help of which no dehydrogenation is possible. Tetrahydroacetophenone, $CH_3 \cdot CO \cdot C_6H_9$, on the other hand, gives the octahydro-*iso*quinoline derivative (IX), with cyanoacetamide both by Michael's as well as Knoevenagel's reactions. Further, it is readily hydrolysed into the corresponding hydroxy-compound (X), without rupture of either of the fused rings, thus showing the stabler nature of partially reduced quinoline rings as compared with the corresponding pyridine rings.

The hydroxy-compound (X) on successive distillation with zinc dust and litharge gives rise to 1-*methyl*-iso*quinoline* (XI), identified by means of its picrate and platinichloride. This provides with an absolutely new method of *iso*quinoline synthesis.

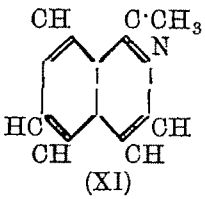
With malonic ester this ketone gives rise to a dihydroxy-hexahydronaphthalene derivative (XII), after the fashion of the formation of dihydroresorcinol derivatives from benzylidene acetone and malonic ester, first recorded by Vorländer (*Annalen*, 1897, **294**, 273).

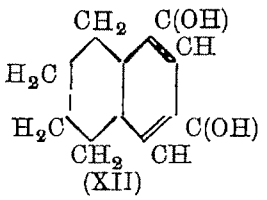


(IX)



(X)


(XI)


(XII)

EXPERIMENTAL.

General Method.—The condensations were carried out with cyanoacetamide both by Michael's and Knoevenagel's reactions as described in the case of arylidene ketones. Only in the present cases the reaction products were not allowed to remain in the reacting (alkaline) medium for any greater length of time than was necessary for the completion of the condensation reaction in order to prevent the formation of the dihydro-derivatives. The small quantity of this latter product that was inevitably formed, specially by the Michael's reaction, was easily separated by digesting the whole reaction product with rectified spirits, in which it was almost insoluble. From the portion soluble in alcohol, the tetrahydro-compound was obtained in a pure state after two or three crystallisations from alcohol till the melting point became constant and sharp. The piperidine reaction product was obtained sufficiently pure when the reaction mixture was worked up within two to three days. Longer duration gave appreciable quantities of the dihydropyridone. Both the condensation products when hydrolysed by concentrated hydrochloric acid in a sealed tube in the usual way, gave the same open-chain acid, which could also be obtained from the reaction product of the corresponding ketone and malonic ester by Michael's method. The Michael product was dehydrogenated as usual by nitrous acid in acetic acid solution, and hydrolysed into the corresponding hydroxypyridine by means of 75 p. c. sulphuric acid in the way described before.

I. *Condensation of Ethylidene Acetophenone with Cyanoacetamide.*

The ketone was prepared by the method of Kohler (*Amer. Chem. J.*, 1909, **42**, 375) from crotonic acid through the intermediary of the bromo-ketone, as direct condensation of crotonyl chloride with benzene by Friedel-Craft's reaction gave a very low yield of the desired product and more of β-phenylbutyrophenone, $Ph{\cdot}CH{\cdot}(CH_3){\cdot}CH_2{\cdot}CO{\cdot}Ph$. The bromo-ketone was debrominated by alcoholic

potassium iodide as this gave a more satisfactory yield than by its reduction with zinc

Michael's Reaction: (I, R=Ph) *Formation of 2-keto-3-cyano-4-methyl-6-phenyl-2:3:4:5-tetrahydropyridine.*—The total condensation product obtained by diluting and acidulating the reaction mixture after two days came to about 90 p. c. of theory, of which about 10 p. c. consisted of the dehydrogenated product, which was left behind when the whole mass was extracted with rectified spirits. The tetrahydropyridone was obtained from the alcohol solution and after three crystallisations from alcohol melted at 248-50°. It had all the properties of its other homologues described previously. (Found: N, 13·51. $C_{13}H_{12}ON_2$ requires N, 13·2 per cent.).

Knoevenagel's Reaction: (VII, R=Ph) *Formation of 2-keto-3-cyano-4-methyl-6-phenyl-6-hydroxypiperidine.*—This compound also was obtained in a very good yield after three days, and was isolated by acidulating the reaction mixture with dilute mineral acids. Crystallised from alcohol it was obtained in fine short needles, m. p. 177-78°. It could be readily dehydrated by gaseous hydrogen chloride in chloroform or carbon tetrachloride suspension in the usual way. (Found: N, 12·43. $C_{13}H_{14}O_2N_2$ requires N, 12·17 per cent.).

Hydrolysis of the Condensation Products: *Formation of β-Methyl-γ-benzoylbutyric Acid.*—This could be easily obtained by hydrolysing any of the above condensation products with concentrated hydrocloric acid in a sealed tube at 120-25° for 3-4 hours. It separated as an oil, which when extracted with ether, dried and evaporated, did not readily solidify, but did so on being left in vacuum over sulphuric acid. Crystallised from a mixture of chloroform and petroleum ether it melted at 72-73°. It was extremely soluble in all solvents excepting petroleum ether and resembled its other homologues in its other properties. (Found: C, 70·05; H, 7·20; M.W. (by titration), 207·5. $C_{12}H_{14}O_3$ requires C, 69·9; H. 6·8 per cent., M.W., 206).

Formation of 3-cyano-4-methyl-6-phenyl-2-pyridone(II, R=Ph).—Apart from the spontaneous formation of this compound, by the Michael's reaction referred to above, it could be easily prepared by treating the tetrahydropyridone with nitrous acid in the usual way. Crystallised from glacial acetic acid or pyridine it was obtained in beautiful cream coloured prisms, that melted at 309-10°, and was identical with a specimen prepared by Basu (*J. Indian Chem.Soc.*, 1930, 7, 488). (Found: N, 13·26. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.).

Hydrolysis of above : *Formation of 2-hydroxy-4-methyl-6-phenylpyridine* (VIII, R=Ph).— This was obtained by heating the above compound with 75 p. c. sulphuric acid till the liberation of carbon dioxide ceased. The hydroxypyridine did not separate on cooling and diluting the acid solution but was obtained on neutralising the same by sodium carbonate. It was extremely soluble in all solvents, insoluble in petroleum ether and cold water, but moderately so in boiling water. Crystallised from 40 per cent. alcohol (charcoal) it was obtained in fine white needles, m.p. 180-81°. It was compared with a specimen from stock, (Basu, *loc.cit.*). It gave a beautiful violet coloration with ferric chloride, and possessed the other properties ascribed to this type of compounds in previous publications. (Found: N, 7·92. $C_{12}H_{11}ON$ requires N, 7·57 per cent.).

Condensation with Malonic Ester : *Formation of α-carboxy-β-methyl-γ-benzoylbutyric Acid, and the action of heat on it.*— The condensation was carried out as usual and the product was directly hydrolysed by dilute potassium hydroxide. The acid that separated as an oil on acidulation was extracted with ether followed by the usual treatments. It was very soluble in all solvents and crystallised from a mixture of chloroform and petroleum ether, m.p. 141-42° (decomp.) and resembled its other homologues in its porperties. (Found: C, 62·15; H, 5·85; M.W. (by titration), 253. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6 per cent., M.W., 250). On being heated at its melting point till effervescence ceased, it was converted into the monobasic keto-acid described above.

II. *Condensation of Ethylidene-p-Methylacetophenone with Cyanoacetamide.*

The ketone was obtained in an exactly similar way as in the previous case, by substituting benzene with toluene in the Friedel-Craft's reaction. *α:β-iDbromo--p-methylbutyrophenone*, $CH_3 \cdot CHBr \cdot CH.Br\ CO.C_6H_4.CH_3$ was prepared now for the first time and was found to resemble its lower homologue in all its properties. Crystallised from dilute alcohol it was obtained in fine white needles, m. p. 120-21°. (Found: Br, 49·65. $C_{11}H_{12}OBr_2$ requires Br, 50·0 per cent.). It was debrominated as in the previous case by alcoholic iodide and resembled its lower homologue in its properties. It was a pale yellow oil that boiled at 222°/16 mm.

The condensations with cyanoacetamide and malonic ester were carried out in an exactly similar manner as in the previous case and

so the condensation products alone have been described here, the experimental details being omitted.

2-Keto-3-cyano-4-methyl-6-p-tolyl-2:3:4:5-tetrahydropyridine (I, R=*p*-tolyl)was obtained in an yield similar to the previous case, mixed with a small quantity of the dihydro-compound, and was separated by treating with alcohol as before. After three crystallisations from alcohol it melted at 255-56°. (Found: N, 12·53. $C_{14}H_{14}ON_2$ requires N, 12·39 per cent.).

2-Keto-3-cyano-4-methyl-6-p-tolyl-6-hydroxypiperidine (VII, R= *p*-tolyl) was obtained by Knoevenagel's method and was isolated after three days. Crystallised from alcohol it melted at 163-64°. It could be readily converted into the Michael compound by dehydration in the usual way. (Found: N, 11·78. $C_{14}H_{16}O_2N_2$ requires N, 11·48 per cent.).

3-Cyano-4-methyl-6-p-tolyl-2-pyridone(II, R=*p*-tolyl) was prepared by treating the tetrahydropyridone with nitrous acid. Crystallised from glacial acetic acid or pyridine it was obtained in white prismatic plates, m. p. 330°, and was identical with a specimen obtained from *p*-toluoylacetone and cyanoacetamide by Basu (*J. Indian Chem.Soc.*, 1931, 8, 124). (Found: N, 12·86. $C_{14}H_{12}ON_2$ requires N, 12·5 per cent.).

2-Hydroxy-4-methyl-6-p-tolylpyridine (VIII, R=*p*-tolyl) was obtained by hydrolysing the above by 75 p. c. sulphuric acid and isolated as in the previous case. Crystallised from dilute alcohol it melted at 183°, and was identical with the specimen described by Basu (*loc.cit., supra*). It gave a violet coloration with ferric chloride. (Found: N, 7·21. $C_{13}H_{13}ON$ requires N, 7·04 per cent.)

α-Carboxy-β-methyl-γ-p-toluoylbutyric acid was obtained by hydrolysing the condensation product between the unsaturated ketone and malonic ester by aqueous potassium hydroxide. Crystallised from a mixture of petroleum ether and chloroform it melted at 125°, (decomp). [Found: C, 63·51; H, 6·32; M.W. (by titration) 262·8. $C_{14}H_{16}O_5$ requires C, 63·64; H, 6·05 per cent., M.W., 264].

β-Methyl-γ- p -toluoylbutyric acid was obtained by heating the above at its melting point for sometime, as well as by hydrolysing any of the original cyanoacetamide condensation products by concentrated hydrochloric acid as in the former case. It solidified on cooling and crystallised from hot water in long colourless needles, m.p. 105-6°. [Found: C,75·68; H. 7·51; M.W. (by titration), 218·2. $C_{13}H_{16}O_3$ requires C, 75·45; H, 7·27 per cent. M.W., 220].

III. *Condensation of Ethylidene Acetone with Cyanoacetamide.*

The unsaturated ketone was prepared from hydracetylacetone [pentanol-(4)-one-(2)-], obtained by condensing acetaldehyde with acetone in presence of potassium cyanide according to the method of Claisen and others, (*Annalen*, 1899, **306**, 322) by dehydration with anhydrous oxalic acid after Pauli and Berg (*Ber.*, 1901 **34**, 2092) as this method gave a better yield than the previously known ones.

2-*Keto*-3-*cyano*-4 : 6-*dimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine* (I, R=Me) was obtained in a good yield when the above ketone was condensed with cyanoacetamide in the usual way by Michael's reaction. The product being very sparingly soluble in all solvents, it was best purified by dissolving in alkali followed by precipitation with dilute mineral acids. It was thereby obtained as a white granular powder, which had no m.p. but sublimed away on being heated. (Found: N, 18·58. $C_8H_{10}ON_2$ requires N, 18·67 per cent.).

2-*Keto*-3-*cyano*-4 : 6-*dimethyl*-6-*hydroxypiperidine* (VII, R=Me) was obtained also in a good yield when the two substances were condensed in presence of piperidine. The substance was isolated as usual and crystallised from alcohol, m.p. 173-75°. (Found: N, 16·85. $C_8H_{12}O_2N_2$ requires N, 16·67 per cent.).

3-*Cyano*-4 : 6-*dimethyl*-2-*pyridone* (II, R=Me) was prerared from the above tetrahydropyridine derivatives by dehydrogenation with nitrous acid in the usual way. It was identified with an identical product obtained by condensing acetylacetone with cyanoacetamide (Basu, *J. Indian Chem. Soc.*, 1930, **7**, 490). Crystallised from dilute acetic acid it melted at 289°. (*cf.* Guareschi, *Atti. R Accad. Sci. Torino*, 1893, **28**, 330, 8370). (Found: N, 19·04, $C_8H_8ON_2$ requires N, 18·92 per cent.).

IV. *Condensation of Mesityl Oxide with Cyanoacetamide.*

Mesityl oxide was prepared from diacetone alcohol, prepared by the self condensation of acetone in presence of barium hydroxide by the method of Conant and Tuttle, "Organic Synthesis", vol. I. p. 45, 53). The condensations were carried out in the usual manner, with the only exception that on account of the solubility of the products in water, they were obtained by evaporating the acidulated reaction

mixtures on the water-bath followed by extraction of the condensation products by alcohol. As has been mentioned in the theoretical part, the same hydroxypiperidine derivative, 2-*keto*-3-*cyano*-4:4:6-*trimethyl*-6-*hydroxypiperidine* was obtained both by Michael's as well as by Knoevenagel's reactions. Crystallised from water or or alcohol it was obtained in colourless prisms, m.p. 278-75°. (Found: C, 59·64 ; H, 7·99 ; N,* 18·4. $C_9H_{14}O_2N_2$ requires C, 59·33 ; H, 7·69 ; N, 15·38 per cent.).

On treating the above compound with gaseous hydrochloric acid in carbon tetrachloride suspension, in the manner described previously, the dehydrated product, 2-*keto*-3-*cyano*-4:4:6-*trimethyl*-2:3:4:5-*tetrahydropyrine* was obtained. On crystallisation from alcohol it melted at 252-54°. (Found: C, 65·53 ; H, 7·51. $C_9H_{12}ON_2$ requires C, 65·85 ; H, 7·31 per cent.). On treatment with nitrous acid both the above compounds were recovered unchanged, showing the stability of this substance towards oxidising agents. (*cf.* Qudrat-i-Khuda, *J. Chem. Soc.*, 1929, p. 201).

V. *Condensation of Tetrahydroacetophenone with Cyanoacetamide.*

The ketone was prepared by Darzen's method (*Compt. rend.*, 1910, **150**, 707) by condensing acetyl chloride with *cyclo*hexene in presence of anhydrous stannic chloride. It was observed that the ketone could be better purified by steam distillation followed by distillation in vacuum, b.p. 95-100°/15-20 mm. *cyclo*hexene was prepared by the method of Coleman and Johnstone from *cyclo*hexanol ("Organic Synthesis)', vol. V. p. 33).

In this case also the reactions (both Michael and Knoevenagel) characterised themselves by yielding the same octahydro-*iso*-quinolone derivatives by both reactions. Further, this compound is easily hydrolysed into the corresponding hydroxy-compound by 75 p. c. sulphuric acid without rupture of any of the two fused rings and yields a methyl derivative quite readily by means of dimethyl sulphate.

Formation of 1-*methyl*-3-*keto*-4-*cyano*-3:4:5:6:7:8:9:10-*octahydro*-iso*quinoline* (IX).—This compound was obtained in an yield

* The high nitrogen figure in the analytical data, is due to the presence of a little methane that invariably comes with the nitrogen when such hydroaromatic bases containing two methyl groups attached to any one carbon atom is combusted with cupric oxide in the ordinary way (Haas, *J. Chem. Soc*, 1906, **89**, 570).

of about 60 p. c. by Michael's reaction and about 50 p. c. by Kneovenagel's reaction. It was nearly insoluble in all solvents excepting glacial acetic acid and pyridine. It resembled the dihydropyridones in all its properties, and crystallised from pyridine in fine white short needles, m.p. 358-60°. (Found: N, 14·97. $C_{11}H_{14}ON_2$ requires N, 14·74 per cent.).

Hydrolysis of the above: *Formation of the Compound* (X).—The hydrolysis was carried out with 75 p. c. sulphuric acid in the usual way when the hydroxy-compound could be obtained by neutralising the diluted solution with sodium carbonate. Crystallised from dilute alcohol it was obtained in fine white felty needles, m. p. 231-32° (decomp.). It dissolved in alkalis quite readily and was precipitated unchanged on acidulation, and gave a reddish-violet coloration with ferric chloride. (Found: N, 8·53. $C_{10}H_{15}ON$ requires N, 8·48 per cent.).

The N-*methyl ether* of the original condensation product (IX) was prepared by dissolving it in aqueous alkali and adding an excess of dimethyl sulphate little by little with good shaking, and keeping the solution alkaline by the addition of alkali from time to time. The mixture warmed up during the operation and soon the methyl derivatives, being no longer soluble in alkali, began to separate, and was fully separated on cooling. It was filtered off, washed till free from alkali and crystallised from dilute alcohol when it was obtained in white felty needles, m. p. 122-23°. (Found: N, 14·03. $C_{12}H_{16}ON_2$ requires N, 13·72 per cent.).

Formation of 1-*Methyl*-iso*quinoline* (XI).—The hydroxy-compound (X) when distilled successively with zinc dust and litharge yields a heavy boiling basic oil. This was purified by extracting non-basic impurities with ether from its acid solution. It was reprecipitated with alkali, extracted with ether, and the free base isolated threfrom; it was a yellow oil with a characteristic quinolinous odour. Its etherial solution when heated with a similar solution of picric acid yielded a *picrate* that crystallised from alcohol in fine yellow needles, m.p. 209-10°. [Found: N, 15·26. $C_{10}H_9N, C_6H_2(NO_2)_3OH$ requires N, 15·06 per cent.].

The *platinichloride* obtained as usual melted at 200-202° (decomp.). [Found: Pt, 27·86. $(C_{10}H_9N, HCl)_2 PtCl_4$ requires Pt, 28·02. per cent.].

Condensation with Malonic Ester: *Formation of* 1:3-*dihydroxy*-5:6:7:8:9:10-*hexahydronaphthalene* (XII).—The condensation

was carried out as usual and the condensation product directly hydrolysed by boiling with dilute aqueous potash, on cooling, the asolution was washed with ether and the hydrolysed product precipitated by acidulating the aqueous solution. It first separated as an oil which finally solidified, and was crystallised from dilute leohol in white, short, prismatic needles, m.p. 115°. (Found: C, 71·35; H, 9·74. $C_{10}H_{16}O_2$ requires C, 71·43; H, 9·52 per. cent.).

The author takes this opportunity of offering his sincerest thanks to Professor H. K. Sen, for his keen interest in the present investigation. His thanks are also due to the Indian Chemical Society for a grant that has defrayed the cost of a few of the chemicals used herein, and to Mr. U. Basu for kindly offering some of his compounds for comparison.

Department of Applied Chemistry,
University College of Science and Technology,
Calcutta.

Received August 15, 1931.

Complexes of Antimony Trichloride with Organic Sulphides.

By Prafulla Chandra Ray, Nadiabehari Adhikari and Amarendra Nath Roy.

In course of the present investigation, several compounds of antimony trichloride with some of the alkyl sulphides have been prepared and their behaviour studied in detail. These include:—

I. $SbCl_3 \cdot Me_2S$.

II. $SbCl_3 \cdot Et_2S$.

III. $SbCl_3 \cdot Pr_2S$.

IV. $4SbCl_3 \cdot 3Bu_2S$.

V. $2SbCl_3 \cdot HCl \cdot 3Et_2S$.

VI. $2SbCl_3 \cdot HCl \cdot 3Bu_2S$.

Antimony trichloride at ordinary temperatures dissolves in the liquid sulphides without any apparent reaction but reacts visibly at elevated temperatures (120°—190°) in sealed tubes. The purification and crystallisation of these compounds require care, as they are sensitive to moisture.

The above compounds fall into two groups: I to IV and V and VI. Compounds (I-IV) are white crystalline substances, soluble freely only in acetone and insoluble in ether, benzene, chloroform and many other non-hydroxylic solvents. The methyl sulphide compound is somewhat exceptional and turns orange-red, when treated with acetone. They are all decomposed by water or alcohols and first turn yellow gradually deepening to orange-red, as the decomposition proceeds. The ultimate product is antimony trisulphide. The yellow or orange-yellow intermediate compounds contain variable percentage of carbon and chlorine, which gradually decreases, as the treatment with water or alcohol is prolonged. The reaction has been studied in detail in the case of the ethyl and butyl sulphide compounds. With warm alcohol, other decomposition products, besides antimony sulphide, are formed and the following have been obtained:—

(*i*) $2\ SbCl_3 \cdot HCl \cdot 3Et_2S$.

(*ii*) $2\ SbCl_3 \cdot HCl \cdot 3Bu_2S$.

With water, these compounds could not be obtained but antimony oxychloride was detected, besides antimony sulphide. Treatment with boiling alcohol also causes similar decomposition.

An attempt was made to replace $SbCl_3$ by some other metallic chloride. An acetone solution of mercuric chloride, added to the compound, $SbCl_3 \cdot Et_2S$ in acetone, throws down at once a white precipitate, having the composition, $Hg_2Cl_2 \cdot Et_2S$. The other compounds react similarly. When treated with thiocarbamide in acetone, a yellow compound slowly crystallised. It was found to be $SbCl_3 \cdot 3CS(NH_2)_2$ (Vanino and Mussgnug, *Ber.*, 1917, **50**, 21).

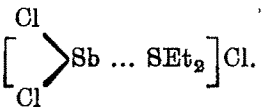
An acetone solution of silver nitrate with a solution of the same solvent gives a reddish-brown precipitate, consisting of antimony sulphide and silver chloride. The precipitation of the sulphide occurs only after the complete removal of chlorine as silver chloride. It is probable that at first a reaction in the sense of the equation, $SbCl_3 \cdot Et_2S + 3AgNO_3 = Sb(NO_3)_3 \cdot Et_2S + 3AgCl$ takes place but the nitrate of antimony, being very unstable, is at once decomposed by ethyl sulphide to antimony sulphide.

When dry ammonia is passed into acetone solutions of these compounds, they decompose. Curiously enough, antimony sulphide was again the principal product of the decomposition. With caustic alkali, all the compounds decompose with the liberation of the respective sulphides.

Constitutional Formula.—From the mode of decomposition with water or alcohol, it seems probable that they are not mere addition compounds. On the addition of water, very little oxychloride is precipitated, the bulk of the compound being decomposed to antimony sulphide. This, as well as the reaction with ammonia, shows that an intimate union exists between the antimony atom and the alkyl sulphide group. It may be mentioned that no antimony sulphide is produced, if $SbCl_3$ and Et_2S are heated together with water. The simplest method of formulation, which suggests itself is $Cl_3 = Sb...SEt_2$. The conductivities are, surprisingly enough, greater than those of antimony trichloride at corresponding dilutions. The fact that all the chlorine is precipitated by silver nitrate in the cold seems to point to the possibility that all the chlorine atoms are ionisable.

The conductivity data in acetone solution, however, indicate that in acetone the compound is ionised into two ions and the molecular weight (184) as determined by the boiling point

method also supports this view. So that in acetone solution, the compound possibly behaves as



It is also possible that the antimony atom co-ordinates one or more acetone molecules, so that the usual co-ordination number 4 or 6 is satisfied. The conductivity values are shown in the following tables.

TABLE I.

Conductivity of $SbCl_3$ *in acetone at* 25°.

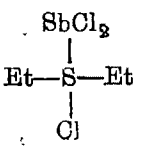
Data obtained by Kahlenberg and Lincoln (*J. Phys. Chem.*, 1899, 3, 12).		Data obtained by the author.	
Dilution.	Mol. conductivity.	Dilution.	Mol. conductivity.
7·07 litres	1·28 r. o.		
14·14	1·55	55·20 litres	2·07 r. o.
28·27	1·83	110·40	3·30
56·56	2·13	220·80	3·81
113·10	3·34		

TABLE II.

Conductivity of $SbCl_3 \cdot Et_2S$ *in acetone at* 25°.

Dilution.	Mol. Conductivity in freshly prepared solution.	Dilution.	Mol. conductivity after 24 hrs.
308 litres	72·77 r. o.	236 litres	74·20 r. o.
616	81·56	472	80·79
1232	86·81	944	86·56
2464	92·30		
4928	94·62		

But a more plausible supposition is that the compounds have a constitution such as



of the sulphonium type. Such a constitution readily explains the conductivity as well as the close relationship between the sulphur and the antimony atoms. However, further investigation is desirable.

The reduction of mercuric chloride to the mercurous stage remains to be considered. This may be due to the tendency of $[Sb...SEt_2]Cl_3$ to pass into $[Sb.SEt_2]Cl_5$ just as K_2PtCl_4 is readily oxidised to K_2PtCl_6.

Compounds (V) *and* (VI).—These are white crystalline substances with sharp melting points and freely soluble in alcohol but moderately so in acetone. With water the solutions decompose and antimony oxychloride is formed. These are additive compounds. Silver nitrate precipitates only silver chloride and hydrogen sulphide precipitates antimony sulphide from solutions of these compounds.

Compounds such as $2SbCl_3 \cdot HCl, 2H_2O$ and $2BiCl_3 \cdot HCl, 3H_2O$ resembling these compounds to some extent are quite well known.

Experimental.

Preparation of $SbCl_3 \cdot Et_2S$.—Antimony trichloride and ethyl sulphide were mixed together in molecular proportions. The trichloride dissolved in the sulphide with evolution of heat. The mixture was then heated in a sealed tube at 140-50° for about six hours. The reaction product, a foul smelling black viscous mass, is insoluble in ether. Consequently the unchanged reactants which were soluble were removed by shaking several times with ether The residue was dissolved in acetone, reprecipitated by ether and the process repeated till it was free from antimony trichloride and ethyl sulphide. It was redissolved in acetone and further purified by refluxing with animal charcoal. On evaporation, a light coloured viscous mass remained behind. In order to obtain it in a crystalline form, the compound was dissolved in a little acetone in a conical flask and ether was added, until a part of the substance was thrown down. The mouth of the flask was then loosely corked up and the vessel left for several days. A mass of tiny white crystals appeared, m. p. 143°.

The reagents and solvents should be free from moisture. With either of the reactants in excess, the same compound was obtained. (Found: C, 14·98; H, 3·31; Sb, 38·35; Cl, 33·51. $SbCl_3 \cdot Et_2S$ requires C, 15·07; H, 3·14; Sb, 38·25; Cl, 33·44 per cent.).

Sulphur is found to be present. The presence of diethyl sulphide is indicated by its smell on warming with caustic alkali.

Preparation of $SbCl_3 \cdot Me_2S$.—The reactants were heated at 120-30° as above. The dark viscous product was at first treated several times with ether. On addition of acetone, the compound gradually decomposed turning orange-yellow. The mass after treatment with ether was left in a vacuum desiccator for several hours, when white crystals gradually separated ; these were washed several times with ether. (Found : C, 8·12; Cl, 37·05; Sb, 42·42. $SbCl_3 \cdot Me_2S$ requires C, 8·29; Cl, 36·81; Sb, 42·10; per cent.). It was insoluble in the solvent.

Preparation of 4 $SbCl_3 \cdot 3\text{-n-}Bu_2S$.—The reactants in the proportion of 2 : 1 were heated at 170-90° as above. The resulting dirty syrupy mass was washed with ether as usual, dissolved in acetone, refluxed with animal charcoal. On evaporation of the acetone, a white granular mass, contaminated with a dirty substance, was obtained. The latter could not be eliminated by repeating the process. On adding a little alcohol in the cold (ice), the dirty oily substance passed into solution leaving behind a perfectly white granular mass. It was dried in a vacuum desiccator and crystallised from acetone.

TABLE I.

	Found.			Calc. for	Calc. for
	I.	II.	III.	$2Sb_2Cl_5(OH) \cdot 3Bu_2S, 2H_2O$.	$2Sb_2Cl_5(OH) \cdot 3Bu_2S$.
Sb,	36·65 36·06	36·95 36·47	36·50	36·09	37·07
Cl,	25·84 25·98	25·98	26·14	26·29	27·02
C,	21·13	—	20·97	21·33	21·92
H,	—	—	4·48	4·44	4·27
S,	—	—	6·54	7·11	7·31

The deficiency of chlorine, as well as the slightly variable percentage of antimony, indicate that the increased hydrolysis beyond the state $Sb_2Cl_5(OH)$ takes place.

It is a white crystalline compound, m.p. 105°. It turns red at the melting temperature. The compound was next prepared in such a way that the presence of water was carefully excluded.

TABLE II.

Found			Calc. for	Calc. for
I.	II.	III.	$2Sb_2Cl_5(OH)\cdot ?Bu_2S$.	$4SbCl_3\cdot 3Bu_2S$.
Sb, 37·55	36·69	36·54	37·07	36·06
Cl, 27·68	28·54	28·87	27·02	31·44
C, 22·34	—	—	21·92	21·80

This compound does not turn red at the melting point. The best results indicate that it is very difficult to avoid hydrolysis by moist air even when dry reagents are used.

$SbCl_3\cdot Pr_2S$ is a white crystalline compound, m.p., 124°. (Found: Sb, 34·91; Cl, 31·02. $SbCl_3\cdot Pr_2S$ requires Sb, 35·14; Cl, 30·75 per cent.).

Preparation of $2SbCl_3\cdot HCl\cdot 3Bu_2S$.—The compound $4SbCl_3\cdot 3Bu_2S$ was added to alcohol and gently warmed for about 2 hours. The orange-red antimony sulphide was removed by filtration and the filtrate left for two or three days, when white crystals were formed. (Found: C, 32·03; S, 9·78; Sb, 26·43; Cl, 27·12. $2SbCl_3\cdot HCl\cdot 3Bu_2S$ requires C, 30·94; S, 10·32; Sb, 26·16; Cl, 26·96 per cent.). It is a white crystalline compound with a sharp melting point at 125°.

Preparation of $2SbCl_3\cdot HCl\cdot 3Et_2S$.—It was prepared exactly as above. It is a white crystalline compound, melts at 75° without apparent decomposition. (Found: C, 18·30; Sb, 31·90; Cl, 32·65. $2SbCl_3\cdot HCl\cdot 3Et_2S$ requires C, 18·87; Sb, 31·93; Cl, 32·57 per cent.).

Preparation of $Hg_2Cl_2\cdot Et_2S$.—An acetone solution of mercuric chloride was added drop by drop to $SbCl_3\cdot Et_2S$ in acetone, until no further white precipitate was formed. The precipitate was filtered and washed several times with acetone.

It is a white amorphous voluminous mass when first prepared, gradually shrinking and hardening with drying; it darkens gradually and turns black after a few days. It is insoluble in the usual solvents but is dissolved by aqua regia, with precipitation of sulphur.

That mercurous mercury is present is shown by treating it with ammonia or caustic alkali, when it turns black. (Found: C, 8·08; Cl, 12·51; Hg, 70·50. $Hg_2Cl_2\cdot Et_2S$ requires C, 8·53; Hg, 71·30; Cl, 12·65 per cent.).

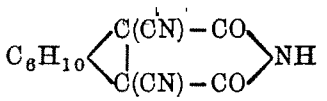
PALIT PROFESSOR'S LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
CALCUTTA,

Received May 11, 1931.

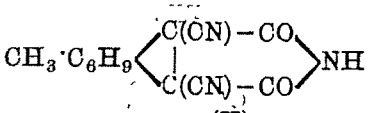
spiro-Compounds. Part I.

By Prafulla Kumar Paul.

Thorpe and his collaborators propounded their memorable "valency deflexion hypothesis" (Beesely, Ingold and Thorpe, *J. Chem. Soc.*, 1915, **107**, 1080) on the basis of their exhaustive study of the relative ease of formation and stability of *cyclo*hexane-*spiro*-*cyclo*propane compounds and *gem*-dimethyl-*cyclo*propane compounds. But the difference in stability of the *spiro*-compounds (I) and (II) as observed by Birch and Thorpe (*J. Chem. Soc.*, 1922, **121**, 1821) seems to be very strange in view of the said "valency deflexion hypothesis" and so the present author has undertaken the study of the formation and stability of different *spiro cyclo*butane derivatives analogous to norpinic acid, with a view to see whether the same kind of difference is to be observed in these cases also, and if so, to what extent could this phenomenon help to settle the question of a strained or strainless configuration of different ring systems.

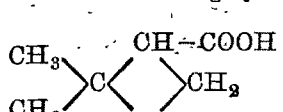


(I)

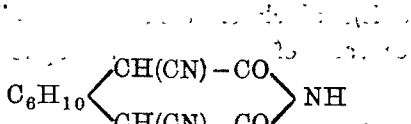


(II)

If according to the suggestion of Sachse (*Ber.*, 1890, **23**, 1363) and Mohr (*J. pr. Chem.*, 1918, *ii*, **98**, 315) *cyclo*hexane were to be a strainless ring then the ease of formation of these *spiro-cyclo*butane compounds would all be of the same order as *gem*-dimethyl compound such as norpinic acid (III) and its derivatives (Kerr, *J. Amer. Chem. Soc.*, 1929, **51**, 614) or else these should differ according to the difference observed by Thorpe and others between the behaviour of *cyclo*hexane and other ring systems.

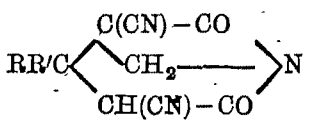


(III)

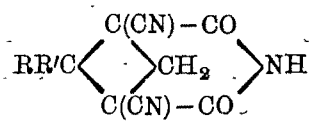


(IV)

With this idea in view, the condensation of methylene iodide with sodio-derivatives of the Guareschi-compounds from *cyclo*hexanone (IV) and other homologous ketones was effected according to the method of Kerr (*loc. cit.*). There was a possibility that the compound (V) could also be obtained in preference to the required product (VI) as it happens in methylating these Guareschi-imides (Kon and Thorpe, *J. Chem. Soc.*, 1922, **121**, 1795) but fortunately the reaction went in the requisite direction yielding the *spiro*-compound (VI) where RR′ are parts of different ring systems, *cyclo*pentane, *cyclo*hexane and substituted *cyclo*hexanes.

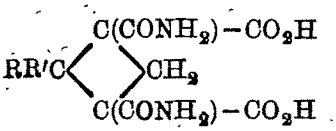


(V)

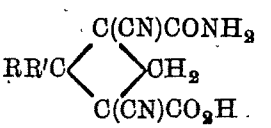


(VI)

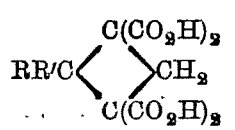
The condensation products on being hydrolysed with alkali of different concentrations gave the compounds (VII), (VIII) and finally the tetracarboxylic acid (IX).



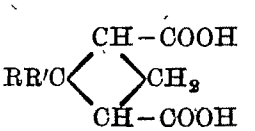
(VII)



(VIII)



(IX)



(X)

The tetracarboxylic acids of the type (IX) appear to behave rather in an anomalous way on being titrated with a solution of baryta, but on being heated to their melting temperatures these acids decompose with the loss of carbon dioxide and yield dicarboxylic acids of the type (X), which exist in both *cis*-and *trans*-configurations.* The silver salts of these tetracarboxylic acids decompose with explosive

* Their separation was effected by taking advantage of the fact that only the *cis*-acid forms an anhydride with acetyl chloride.

violence and so these experiments could not be relied upon but analysis gave results in complete accord with the tetracarboxylic acid structure. Such anomaly of behaviour on baryta titration has also been observed by Kerr (*loc. cit.*).

In conclusion the *spiro-cyclo*butane compounds described in the present paper have been found to correspond very closely to norpinic acid and its derivatives as regards their stability and ease of formation. The yield of the condensation product of methylene iodide with sodio-derivative of Guareschi-imide described in the present paper approximates very closely to that of dicyanonorpinimide of Kerr (*loc. cit.*) and the *spiro-cyclo*butane compounds have been found to be as stable as norpinic acid derivatives towards prolonged treatment with boiling caustic alkali. And moreover, these *spiro-cyclo*butane dicarboxylic acids lack remarkably in their tendency to crystallise, so much so, that some of them have not been obtained in crystalline condition, which reminds of the *spiro-cyclo*propane compounds derived from strain-free substances (Backer and Thorpe, *J. Chem. Soc.*, 1920, **117**, 1579; Baker and Ingold, 1928, **123**, 122). These facts in conjunction with an approximate similarity in stability of the substituted *cyclo*hexane *spiro-cyclo*propane compounds and other *spiro-cyclo*propane compounds associated with strain-free substances (*J. Chem. Soc.*, 1921, **119**, 1319; 1922, **121**, 1823, etc.) strongly suggest the substituted *cyclo*hexane ring to be strainless.

But a more conclusive proof of the strain-free character of substituted *cyclo*hexane must be sought in the substituted *cyclo*hexane-*spiro-cyclo*pentane and the corresponding *spiro-cyclo*hexane compounds, the formation of which on the basis of the strain hypothesis (*J. Chem. Soc.*, 1915, **107**, 1980) is quite improbable, the effect of overlapping being of a very pronounced character (*J. Chem. Soc.*, 1922, **121**, 499) and so the author is engaged with the condensation of ethylene bromide and trimethylene bromide with Guareschi-compounds from cyclic ketones and the results already obtained appear to be of interest. These are reserved for a future communication.

EXPERIMENTAL.

Condensation of Guareschi-imide with Methylene Iodide.—Guareschi-imide (1 mol.) was heated with sodium methoxide (3 mols.) in absolute methyl alcohol (1000 c.c.) under reflux on an water-bath for half an hour to yield the disodium derivative. To the

disodium derivative of the Guareschi-imide, methylene iodide (1·5 mols.) was added and the heating continued for 2-3 hours when almost the whole of methylene iodide dissolved and the reaction was complete. The reaction mixture was then cooled and poured into water (2000 c.c.) containing pure nitric acid (200 c.c.), when the condensation product was precipitated. It was then filtered, dried and washed repeatedly with ether to remove adhering methylene iodide and crystallised from glacial acetic acid. The yield of the condensation product varies from 60-65 p.c.

cyclo*Pentane*-1:1-spiro-*dicyan*cyclo*butane Imide*. [*Formula* VI, $RR' = (CH_2)_4 <$].—Disodium derivative of the Guareschi-imide (10·8 g.) derived from *cyclo*pentanone was condensed with methylene iodide (20 g.). It crystallises in needles from glacial acetic acid, m. p. 257°. (Found: N, 18·27. $C_{12}H_{11}O_2N_3$ requires N, 18·34 per cent.).

cyclo*Hexane*-1:1-spiro-*dicyan*cyclo*butane Imide*. [*Formula* VI, $RR' = (CH_2)_5$]. — Guareschi-imide (23 g.) from *cyclo*hexanone was converted into its disodium derivative by treatment with sodium (6·9 g.) in absolute methyl alcohol (100 c.c.) and condensed with methylene iodide (40 g.), and the condensation product after usual treatment, crystallised from glacial acetic acid, m.p. 266°. (Found: N, 17·42. $C_{13}H_{13}O_2N_3$ requires N, 17·28 per cent.).

4-*Methyl*-cyclo*hexane*-1:1-spiro-*dicyan*cyclo*butane Imide*.— Disodium derivative of the Guareschi-imide (24·5 g.) from 4-methyl *cyclo*hexanone was prepared and condensed with methylene iodide (40 g.) and the condensation product after preliminary purification crystallised from glacial acetic acid in needles, m.p. 252°. (Found: N, 16·3. $C_{14}H_{15}O_2N_3$ requires N, 16·34 per cent.).

3-*Methyl*cyclo*hexane*-1:1-spiro-*dicyan*cyclo*butane Imide*.—Methylene iodide (40 g.) and disodium derivative of Guareschi-imide from 3-methyl *cyclo*hexanone (24·5 g.) were condensed in the usual way and the condensation product crystallised from glacial acetic acid, m.p. 259°. (Found: N, 16·3. $C_{14}H_{15}O_2N_3$ requires N, 16·34 per cent.).

Partial Hydrolysis of the Condensation Product of the type (VI). The condensation product (VI) (1 mol.) was dissolved in 10 p. c. potassium hydroxide solution (560 c.c.) and boiled for 5 minutes. The reaction product after cooling and extraction with ether to remove neutral product of reaction was acidified with hydro-

chloric acid and extracted with ether. The ethereal extract was then washed with sodium bicarbonate solution, the bicarbonate-wash on acidification with hydrochloric acid gave the required acid of the type (VIII) as a thick oil which soon solidified and was crystallised from a suitable solvent (yield generally 80 p.c.).

cyclo*Pentane*-1:1-spiro-2′:4′-*dicyan*-2′-*carbamyl*cyclo*butane*-4′-*carboxylic Acid*. (*Formula* VIII, RR′=$(CH_2)_4<$]. —The condensation product (4·6 g.) was treated with 10 p.c. potassium hydroxide solution (11·5 c.c.) for 5 minutes, and the product of reaction after usual treatment crystallised from ethyl acetate in prismatic needles, m.p. 188°. (Found: N, 17·05 $C_{12}H_{13}O_3N_3$ requires N, 17 per cent.).

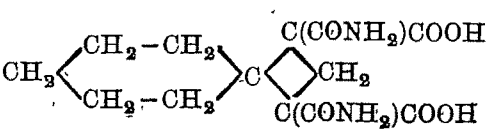
4-*Methyl*-cyclo*hexane*-1:1-spiro-2′:4′-*dicyan*-2′ *carbamyl*-cyclo*butane*-4′-*carboxylic Acid*.

(*Formula* VIII, RR′=MeCH$\begin{pmatrix}CH_2\cdot CH_2\text{-}\\ CH_2\cdot CH_2\text{-}\end{pmatrix}$.

The condensation product (12·8 g.) was hydrolysed with 28 c.c. of 10 p.c. potassium hydroxide solution for 5 minutes and after preliminary purification crystallised from dilute alcohol, m.p. 204°. (Found: N, 15·47. $C_{14}H_{17}O_2N_3$ requires N. 15·27 per cent.).

3-*Methyl*-cyclo*hexane*-1:1-spiro-2′:4′-*dicyan*-2′-*carbamyl*cyclo *butane*-4′- *carboxylic Acid*. (Formula VIII, RR′=$-CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2-$).— 3- Methyl-*cyclo*hexane-1:1-*spiro*-dicyan*cyclo*butane imide (12·8 g.) on hydrolysis with 10 p.c.c austic potash (28 c.c.) gave the required acid crystallisable in needles from dilute alcohol, m.p. 211°. (Found: N, 15·49. $C_{14}H_{17}ON_3$ requires N, 15·27 per cent.).

cyclo*Hexane*-1:1-spiro-cyclo*butane*-2′:4′-*dicarbamyl*-2′:4′-*dicarboxylic Acid*. VII, RR′=$(CH_2)_5<$.



*cyclo*Hexane-1:1-*spiro*-dicyan*cyclo*butane imide (VI) (12 g.) was dissolved in 2 p.c. caustic soda solution (200 c.c.) and boiled under reflux for 2 hours, when evolution of ammonia ceased. The reaction product was then cooled and acidified with dilute sulphuric acid, when on stirring the acidified solution with a glass rod the required dicarbamyl dicarboxylic acid separated. It was then filtered, dried and crystallised from methyl alcohol, m.p. 180° (decomp.). (Found: N, 9·76. $C_{13}H_{18}O_6N_2$ requires N, 9·39 per cent.).

Complete Hydrolysis of (VII) *and* (VIII) *to* IX.—The compound (VII) or (VIII) was completely hydrolysed by boiling the same (1 mol.) with 20 p.c. sodium hydroxide solution (15-20 mols.), under reflux, on a sand-bath until evolution of ammonia ceased. The completion of the reaction generally takes 20-24 hrs. The reaction mixture was then cooled and acidified strongly with concentrated hydrochloric acid; suspended impurities removed by filtration and the filtrate extracted with ether many times. The ethereal extract on evaporation of ether gave the required tetracarboxylic acid as an oil which solidified on scratching with a glass rod, which was then crystallised from requisite solvent (yield 20 p.c.).

cyclo*Pentane*-1:1-spiro-cyclo*butane*-2′:2′:4′:4′-*tetracarboxylic Acid* [IX, $RR' = (CH_2)_4$ <]. —*cyclo*Pentane-1:1-*spiro*-2′:4′-dicyan*cyclo*butane 2′-carbamyl-4′-carboxylic acid (10 g.) was boiled under reflux with 20 p.c. caustic soda solution (200 c.c.) for 12 hours, and the tetracarboxylic acid separated as usual and crystallised from acetone and petroleum ether, m.p. 190° (decomp). (Found: C, 50·23; H, 5·12. $C_{12}H_{14}O_8$ requires C, 50·35; H, 4·89 per cent.).

cyclo*Hexane*-1:1-spiro-cyclo*butane*-2′:2′:4′:4′-*tetracarboxylic Acid* [IX, $RR' = (CH_2)_5$ <]. —*cyclo*Hexane-1:1-*spiro*-2′:4′-dicarbamyl *cyclo*butane-2′:4′-dicarboxylic acid (10 g.) was hydrolysed with a large excess of 20 p.c. sodium hydroxide as usual for 20-25 hours and the product was crystallised from acetone and petroleum ether in needles, m.p. 190° (decomp.). (Found: C, 51·59; H, 5·83. $C_{13}H_{16}O_8$ requires C, 52·0; H, 5·33 per cent.).

4-*Methyl*-cyclo*hexane*-1:1-spiro-cyclo*butane*-2′:2′:4′:4′-*tetracarboxylic Acid* [IX, $RR' = MeCH(CH_2{\cdot}CH_2)_2$]. —4-Methyl-*cyclo*hexane 1:1-*spiro*-2′:4′-dicyan*cyclo*butane-2-carbamyl-4′-carboxylic acid requires 20-24 hours for complete hydrolysis. The product of hydrolysis

crystallised in needles from formic acid, m.p. 162° (decomp.). (Found: C, 53·18; H, 6·06. $C_{14}H_{18}O_8$ requires C, 53·51; H, 5·78 per cent.).

3-Methyl-cyclohexane-1:1-spiro-cyclobutane-2′:2′:4′:4′-tetracarboxylic Acid (IX, RR′ = $-CH_2-CH_2-CH_2\cdot CHMe-CH_2-$).—3-Methyl-*cyclo*hexane-1: 1-*spiro*-2′:4′-dicyan*cyclo*butane-2′-carbamyl-4′-carbamylic acid (10 g.) was hydrolysed in the usual way for 24 hours, the product of hydrolysis separated and crystallised from acetone and benzene in needles, m.p. 173°. (Found: C, 53·47; H, 6·28. $C_{14}H_{18}O_8$ requires C, 53·51; H, 5·73 per cent.).

Decarboxylation of (IX) *to* (X).—The tetracarboxylic acid of the type (IX) was very cautiously heated in a large test tube in an oil-bath within 5° above the melting point of the tetracarboxylic acid so long as there was evolution of carbon dioxide, with stirring, care being taken that the contents of the test tube did not froth up above the surface of the oil-lench. When there was no more evolution of carbon dioxide the reaction product was cooled and dissolved in freshly distilled acetyl chloride and the acetyl chloride allowed to evaporate in the cold over caustic potash. The reaction product was then taken up in ether and washed twice with sodium bicarbonate solution. The ethereal solution on being dried and evaporated, yielded the anhydride of the *spiro*-dicarboxylic acid (*cis*), as a thick oil. It solidified in a vacuum desiccator in course of time and was crystallised from proper solvent. The yield was very poor. The bicarbonate wash on acidification gave the *spiro-cyclo*butane-*trans*-dicarboxylic acid as a thick oil which was extracted with ether, dried and ether evaporated when the *trans-spiro*-acid was obtained as a gum which solidified in course of time when kept under reduced pressure over sulphuric acid, and crystallised from suitable solvent.

cycloHexane-1:1-spiro-cyclobutane-2′:4′-dicarboxylic Acid (trans) [X, RR′ = $(CH_2)_5<$].—The acid as obtained direct from the reaction product, is a gum and solidified after three days when kept in a desiccator under reduced pressure, and then crystallises in needles from ether, m.p. 178°. (Found: C, 61·9; H 7·74; equivalent, 108. $C_{11}H_{16}O_4$ requires C, 62·7; H, 7·54 per cent.).

Anhydride of cyclohexane-1:1-spiro-cyclobutane-2′:4′-dicarboxylic Acid (cis).—The anhydride solidified in the desiccator after two weeks, it crystallises from benzene in fine elongated needles, m.p. 159-62°. (Found: C, 68·13; H, 7·6. $C_{11}H_{14}O_3$ requires C, 68·05; H, 7·21 per cent.).

*Anhydride of 4-Methyl-*cyclo*hexane-*1:1-spiro-cyclo*butane-2':4'-dicarboxylic Acid* (cis).—The anhydride solidified in the desiccator after three months, and it crystallised from a mixture of ethyl-acetate and petroleum ether in short stout needles, m.p. 180°. (Found: C, 68·82; H, 7·76. $C_{12}H_{16}O_3$ requires C, 19·28; H, 7·69 per cent.).

*3-Methyl*cyclo*hexane-*1:1-spiro-cyclo*butane 2':4'-dicarboxylic Acid* (trans). (X, $RR' = -CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2-$).—The acid solidified in a week and it crystallised from a mixture of acetone and petroleum ether in needles, m.p. 176°. (Found: C, 63·92; H, 7·93. $C_{12}H_{18}O_4$ requires C, 63·72; H, 7·96 per cent.).

My grateful thanks are due to Prof. P. C. Mitter for his kind interest in the work and for placing all the facilities of his laboratory at my disposal.

University College of Science,
Calcutta.

Received January 19, 1931.

Period of Induction of Chemical Reactions. Part II. Action of Hypophosphorous Acid on Sodium Iodate.

By Panchanan Neogi and Binayendranath Sen.

The liberation of iodine by the reduction of iodates by hypophosphorous acid has been mentioned by Vitali(*Boll. Chim. farm.*, 1899, **38**, 201) but we have observed that appreciable time elapses before the liberated iodine makes its appearance ; the conditions and causes governing this induction period, *viz.*, the influence of dilution, temperature, light etc., form the subject-matter of the present communication. The belated appearance of iodine as judged by the period of induction is, in all probability, due to successive reactions in the oxidation of the iodate to the ultimate product namely iodine.

Experimental.

Solutions of sodium iodate and hypophosphorous acid were prepared and their concentrations determined iodometrically (*cf.* Sutton, Volumetric Analysis). The stock solutions were diluted according to requirement. Boiling tubes containing 10 c. c. of each solution were kept before a white back-ground in a thermostat, regulated to the required temperature and when the solutions had acquired the temperature of the bath, the iodate solution was poured quickly into the hypophosphorous acid solution, stirred once and the time before the appearance of iodine noted by means of a stop-watch. A starch solution was employed to indicate the appearance of iodine but it was abandoned, because the blue colour took considerable time to develop.

In the following tables C_h represents the concentration of hypophosphorous acid and C_i that of the iodate in g. moles per litre and T, the induction period in seconds.

Table I.

	Temp. = 28°·4.			$K = T \times C_i \times 10^2$.				$C_h = \cdot 249$.		
C_i	... ·0162	·0324	·0435	·0647	·0807	·0969	·1133	·1792	·1290	·145
T	... 360	180	195	91	73	60·4	52	33	48	39·8
K	... 58·32	58·32	58·72	58·87	58,91	58·52	58·91	58·41	58·65	58·00

The induction period varies inversely as the concentration of the iodate, that of the acid remaining constant.

TABLE II.

Temp. = 28°·2. $K = T \times C_k \times 10$. $C_a = \cdot 0162$.

C_k	... ·00996	·0133	·0149	·0179	·0199	·0218	·0239	·0249	·0278
T	... 199	142·4	135	110	100	90	84	78	70
K	... 19·92	18·94	19·11	19·71	19·90	19·62	19·08	19·52	19·46

The induction period varies inversely as the concentration of the acid, that of the iodate remaining constant.

Thus the induction period varies inversely as the concentration of the acid as also that of the iodate. This conclusion was verified by further experiments, in which concentrations of both were varied; this will be evident from Fig. 1, in which concentration of the mixed solution is plotted against the time.

FIG. 1.

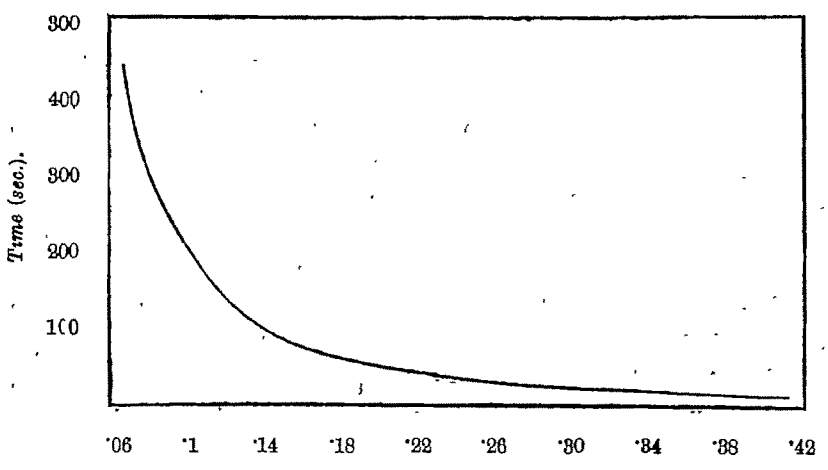


TABLE III.

Influence of Temperature.

"A"

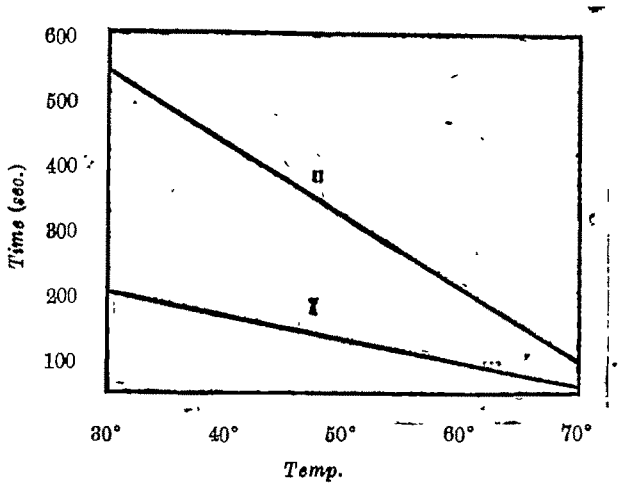
$C_k = \cdot 0249$. $C_a = \cdot 0323$.

Temp.	... 30°	35°	40°	45°	50°	55°	60°	65°	70°
T	... 160	147	128	107	90	72	50	27	8
Temp. coeff.	...	4·2	3·8	4·2	3·4	3·6	4·4	4·6	4·0

"B"

	$C_k = \cdot0253$.					$C_k = \cdot0498$.			
Temp.	... 30°	35°	40°	45°	50°	55°	60°	65°	70°
T	... 539	478	420	360	298	230	168	110	58
Temp. coeff.	...	12	11·6	12	12·4	13·8	12·4	11·6	12·4

FIG. 2.



Thus the period of induction diminishes regularly with increasing temperature.

Influence of Alcohols.—Measured volumes of different alcohols were introduced into the boiling tubes containing the acid, kept in the thermostat. The iodate solution at the same temperature was quickly poured into the mixture, which was then stirred.

TABLE IV.

$C_k = \cdot0248$.						$C_k = \cdot0506$.						
Ethyl alcohol (c.c.)	...	0	1	2	4	6	8	10				
T (Temp. = 27°)	...	89	178	220	300	398	525	630				
Methyl alcohol (c.c.)	...	0	1	2	4	6	8	10				
T (Temp. = 27°·4)	...	89	74	62	55	49	40	28				
iso-propyl alcohol (c.c.)	...	0	1	2	4	6	8	10				
T (Temp. = 27°·4)	...	89	100	312	390	471	585	720				
n-Propyl alcohol (c.c.)	...	0	·5	1	2	3	4	5	6	7	8	9	10
T (Temp. = 28°)	...	89	No appearance of colour of iodine even after 1800 sec.										

Ethyl alcohol lengthens the induction period considerably, whilst methyl alcohol shortens it. This contradictory behaviour of the alcohols is not understood on the basis of polarity and associative power of the two solvents and probably viscosity enters into the phenomenon. Of the two isomeric propyl alcohols, *n*-propyl alcohol lengthens the induction period so enormously that no iodine appears even after the lapse of half an hour and this remarkable divergence may be utilised as a qualitative method of differentiating the two isomeric alcohols.

TABLE V.

Influence of Butyl Alcohols.

C_k = ·0433.			C_i = ·0249.			Temp. = 28°·6.	
n-Butyl alcohol (c.c.)	...	0	1	*iso*-Butyl alcohol	...	0	1
T	...	178	312	*T*	...	178	81

The above experiments were performed in order to examine if the structure of the isomeric alcohols contribute to the peculiar results obtained with the two isomeric propyl alcohols. The limited solubility of the butyl alcohols stood in the way of extension of observation with these. The results show that the effect exerted by these alcohols is of a complicated nature.

TABLE VI.

Effect of Glycerol.

C_k = ·0249.			C_i = ·506.					Temp. = 26°·8.
Glycerol (c.c.)	...	0	1	2	4	6	8	10
T	...	95	140	190	290	400	490	598

Glycerol thus increases the period of induction, in conformity with our previous observations (Neogi and Neogi, *J. Chem. Soc.*, 1927, p. 30; Neogi and Mukherji, *J. Indian Chem. Soc.*, 1229, **6**, 529).

TABLE VII.

Effect of Salts.

$C_k = \cdot0249$. $C_i = \cdot0506$. Temp. = 28°·4.

Salt.	Conc. (*N*).	*T*.	Salt.	Conc. (*N*).	*T*.
Potassium chloride ...	1·5583	152	Potassium citrate ...	·3298	194
Sodium chloride ...	,,	151	Sodium citrate ...	,,	191
Potassium nitrate ...	1·3431	168	Potassium sulphate ...	1·8946	162
Sodium nitrate ...	,,	159	Sodium sulphate ...	,,	160
Potassium tartrate ...	·3109	180	Without salt ...	—	87
Sodium tartrate ...	,,	175			

The period of induction is thus influenced specifically by each kind of salt and the influence appears to be due to anions and independent of cations.

The effect of sugars was next investigated. It was found that cane sugar practically exerts no influence, while grape sugar, fruit sugar and mannose slightly increase the period of induction.

TABLE VIII.

Effect of Geometrical and Optical Isomers.

$C_k = \cdot249$. $C_i = \cdot0339$. Temp. = 28°·4

Isomer.	Conc. (*N*).	*T*.
—	—	189
Maleic acid ...	·06531	207
Fumaric acid ...	,,	224
d-Tartaric acid ...	·7787	255
l-Tartaric acid ...	,,	285

The induction period is influenced to a greater extent by fumaric than by maleic acid at the same concentration. *l*-Tartaric acid has a greater effect than *d*-tartaric acid.

Effect of Solvents.

The effect of solvents of iodine, which are themselves insoluble in water, was next investigated. Carbon tetrachloride, benzene, chloroform, *o*-xylene, *m*-xylene, *p*-xylene and carbon disulphide were tried. These were found to diminish the induction period considerably and the comparative influences appear to follow the order of solubility of iodine in these solvents, as would be seen from the following table.

TABLE IX.

$C_k = \cdot0323$.		$C_i = \cdot0288$.						
		Temp. = 27°·7.						
Carbon tetrachloride (c.c.)	...	0	1	2	4	6	8	10
T	...	212	155	92	44	40	32	21
		Temp. = 27°·5.						
Carbon disulphide (c.c.)	...	0	1	2	4	6	8	10
T	...	213	177	152	110	80	60	50
		Temp. = 28°.						
Benzene (c.c.)	...	0	1	2	4	6	8	10
T	...	210	126	105	74	52	30	10
		Temp. = 28°.						
Chloroform (c.c.)	...	0	1	2	4	6	8	10
T	...	210	146	97	74	60	48	36

TABLE X.

Influence of Acids.

$C_1 = ·0249$.		$C_2 = ·162$.						Temp. = 28°·6.
·0521 *N*-HCl (c.c.)	...	0	1	2	4	6	8	10
T	...	360	300	260	215	170	130	105
·0168 *N*-H_2SO_4 (c.c.)	...	0	1	2	4	6	10	
T	...	360	325	292	255	231	215	

Inorganic acids diminish the period of induction considerably, which is quite unexpected, for the hydrogen ions from these acids should suppress the ionisation of hypophosphorous acid, prolonging the induction period. This can be reconciled by postulating two forms of hypophosphorous acid, ' active ' and ' passive ' in equilibrium with one another—$H_3PO_2 \rightarrow H_5PO_3$. This reaction has been shown to be catalysed by hydrogen ions (Mitchell, *J. Chem. Soc.*, 1921, **119**, 1266; *ibid.*, 1922, **121**, 1624), so that with the addition of acids more of the active forms was formed, thus shortening the induction period.

TABLE XI.

$C_1 = ·0249$. $C_2 = ·0645$. Temp. = 28°.

1 C.c. of the respective reagents was added at each experiment.

Reagent.		C one.	*T*.
Potassium permanganate	...	·005 *N*	92
Hydrogen peroxide	...	—	90
Ammonium persulphate	...	10 p.c.	95
Potassium dichromate	...	·005 *N*	95

As some of the reagents are coloured and as the results are comparative, two drops of starch solution were added to indicate the appearance of iodine. It will be seen that oxidising agents have very little effect on the induction period, a result which is in harmony with the observations of Burgess and Chapman (*J. Chem. Soc.*, 1906, **89**, 1402) in the case of the photochemical induction between hydrogen and chlorine.

Influence of Finely Divided Metals.—The effect of finely divided metals was next investigated. It was found that these reduce the period of induction greatly; the different metals studied stand in the order, Mg $\geq$ Al $\geq$ Zn $\geq$ Ni.

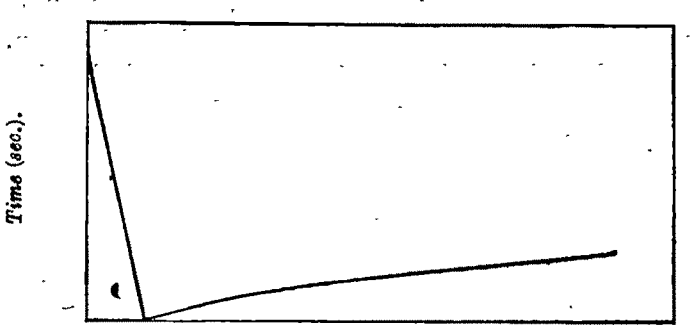
TABLE XII.

Influence of Thiosulphate.

C_A = ·0323. C_I = ·0288. Temp. = 29°.

Thiosulphate conc. (N) ...	0	·0125	·025	·05	·1	·5	1
T ...	215	57	38	25	15	6	

FIG. 3.



It may be mentioned that a similar instance of thiosulphate enhancing the speed of chemical reaction has been observed by Judson and Walker (*J. Chem. Soc.*, 1898, **73**, 410) in the reaction between HBr and $HBrO_3$. The readiness of the appearance of iodine was enhanced by the addition of a little ammonium chloride to the reaction mixture. For instance, 2 drops of N-$Na_2S_2O_3$ gave an induction period of two seconds but previous addition of about 1 g. of NH_4Cl caused the induction period to disappear. Probably sodium iodate, in presence of ammonium chloride, oxidises sodium thiosulphate to tetrathionate, liberating a small quantity of iodine (Jörgensen, *Z. anorg. Chem.*, 1898, **19**, 18). A portion of the added thiosulphate is converted into tetrathionate and iodide and the iodic acid

(iodate in presence of hypophosphorous acids) present in excess gives rise to iodine (Reigler, *Z. anal. Chem.*, 1896, **35**, 308). The small quantity of iodine thus liberated is taken by thiosulphate and more and more iodine is produced. This explains the apparent anomaly.

TABLE XIII$_g$

Influence of Thiosalts.

C_A = ·0249. C_t = ·0645. Temp. = 29°·2.

1 C.c. of the reagent was used at each experiment.

Reagent.	Conc. (N).	T.
Ammonium thiocyanate ...	·05	6
Sodium tetrathionate ...	·05	3
Without addition ...	—	90

TABLE XIV.

C_A = ·0288. C_t = ·0323. Temp. = 29°·2

Conc. of KI = ·1854 N.

Vol. of KI soln. (c.c.) ...	0	0·5	1	2	3	4	5
T ...	212	109	81	58	32	14	nil.

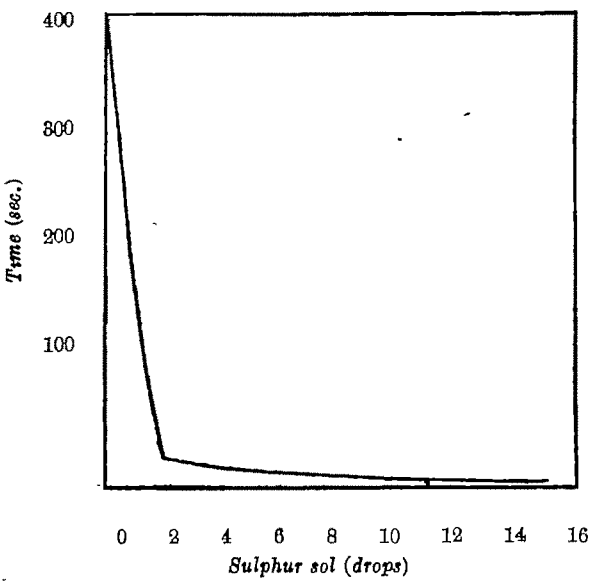
Thus potassium iodide, *added previously to the reaction mixture*, reduces the induction period considerably, the reduction being proportional to the concentration of the iodide. An observation, somewhat similar to this, has been made by Purakayastha (*J. Indian Chem. Soc.*, 1928, **5**, 726), who found that in the case of photochemical induction between bromine and tartaric acid, potassium bromide added to the system previously considerably reduced the induction period.

Influence of Colloidal Sulphur Sol.—The sulphur sol was prepared by Raffo's method, by the interaction of sulphuric acid and sodium thiosulphate followed by dialysation.

TABLE XV.

$C_k = ·0249.$		$C_s = ·0147.$						Temp. = 29°.
Sulphur sol (drops)	...	0	2	4	6	8	10	15
T	...	396	22	15	10	6	3	0

FIG. 4.



Sulphur sol has thus a marked effect on the induction period. This cannot be readily explained but it should be remembered that sulphur is more exceptional in its adsorbability and chemical reactivity amongst colloidal sols.

TABLE XVI.

Influence of Platinum Black and Animal Charcoal.

$C_k = ·0249.$		$C_s = ·0645.$	Temp. = 28°·4.
Substance.		Wt.	T
—		—	93
Platinum black	...	·1 g.	7
Animal charcoal	...	·1	12

Animal charcoal reduces the induction period to a marked extent, to which apparently no single cause may be adduced. Platinum black probably exerts such a decreasing influence by the liberation of hydrogen in the nascent state by reacting with NaH_2PO_2 formed in the course of the reaction, which acts much in the same way as in the case of the action of the finely divided metals on the induction period.

Critical Concentration and Period of Induction.— The process followed consisted in altering the concentration of one of the reactants, the concentration of the other being fixed and observing the induction period, until a concentration was obtained, at which there was no period of induction and iodine appeared immediately.

TABLE XVII.

$C_1 = \cdot0172$.				Temp. = 29°.	
C_2... 1826	·3652	·5478	·7304	·9130	greater than ·9130
T... 6	3·4	2·0	1·4	less than 1 sec.	0

Influence of Light.— Solutions of sodium iodate and hypophosphorous acid were prepared in a dark room, provided with a ruby lamp. Two drops of starch solution (·5 g. of starch in 50 c.c. water) were added to indicate the colour. Since the results were meant for comparison only, the period of induction between starch and iodine did not vitiate the observed effects.

TABLE XVIII.

$C_1 = \cdot0249$.	$C_2 = \cdot0839$.	Temp. = 280·2.
	T	
In Light ...	190	
In Dark ...	189	

Thus the induction period is not influenced by light.

Summary.

(1) The reaction between sodium iodate and hypophosphorous acid has a considerable period of induction, in so far as iodine appears after the lapse of considerable interval from the initial time of mixing the solutions and the period of induction is not influenced by light.

(2) The period of induction is dependent on the dilution of the reactants, the higher the dilution, the greater is the period of induction. Thus the following relations have been found to hold good:

$K = T \times C_h$, when C_h *i.e.* the acid conc. is const.

$K = T \times C_i$, ,, C_i *i.e.* the iodate conc. is const.

$K = T \times C_h \times C_i$, ,, both C_h and C_i are varied,

T, being the period of induction and K, a specific const, for each case.

(3) Increase in temperature causes a decrease in the period of induction.

(4) Of the alcohols, ethyl alcohol causes an increase in the period of induction, while methyl alcohol produces the reverse effect. *n*-Propyl alcohol totally inhibits the reaction, while *iso*-propyl alcohol increases the induction period. The *n*- and *iso*butyl alcohols behave similarly.

(5) The period of induction increases in presence of glycerol, chlorides, sulphates, nitrates, citrates, tartrates, glucose, laevulose and mannose.

(6) The period of induction diminishes in presence of solvents of iodine like carbon tetrachloride, benzene, carbon disulphide, hexane, toluenes and chloroform, the diminution being greatest in the case of benzene and least in the case of carbon disulphide.

(7) Optical isomers like *d*-tartaric acid and *l*-tartaric acid and geometrical isomers like maleic and fumaric acids have considerable influence on the induction period, *l*-tartaric acid, and fumaric acid causing greater increase in the induction period than *d*-tartaric acid and maleic acid respectively.

(8) The presence of dilute mineral acids causes a decrease in the period of induction.

(9) Sodium thiosulphate, even in minute quantities, causes a remarkable diminution in the period of induction and in certain concentrations causes complete disappearance of the induction period. Ammonium thiocyanate and sodium tetrathionate act in a similar manner.

(10) Potassium iodide causes considerable diminution in the induction period and under certain circumstances causes it to disappear altogether.

(11) Colloidal sulphur sol markedly causes diminution of the period of induction.

(12) Oxidising agents have generally little influence on the induction period.

(13) Reducing agents and finely divided metals cause a decrease in the period of induction.

(14) Platinum black and animal charcoal exert marked influence in diminishing the period of induction.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.

Received May 4, 1931.

Compounds of Metallic Salts with Organic Sulphides.

By Sir P. C. Rây, Kt., C.I.E., D.Sc., Ph.D.

In this annual address I would like to give a brief account of the work that is being done in my laboratory for the last few years. This deals with a study of the formation, properties and constitution of the molecular compounds of various metallic salts with organic sulphides and sulphonium halides. Reactions with salts of platinum, gold, silver, mercury, antimony, cadmium and zinc have been studied with this purpose.

Hydrochlorplatinic acid and platinum tetrahalides on treatment with mercaptans, sulphides and disulphides have been found to yield a large variety of compounds with unique properties, whose constitution it is very difficult to explain on the basis of our prevailing conceptions of valency. An explanation has been, however, suggested by the present author on the assumption of variability of the valency of platinum combined with the tendency of the sulphur atom of the sulphides and disulphides to form sulphonium derivatives (*Z. anorg. Chem.*, 1929, **178**, 329; 1930, **187**, 33; 1931, **198**, 53). This tendency of the sulphur atom, as we shall presently see, may be regarded as the underlying "motif" in the formation of many of these molecular compounds of metallic salts with organic thio-compounds. In others, the existence of double or complex compounds of metallic salts with the corresponding sulphonium salts, have been proved, the sulphonium salts being formed during the course of the reaction.

By the interaction of alkyl sulphide, disulphide or trisulphide with ethyl iodide and mercuric iodide, compounds of the type $R_3SI \cdot HgI_2$ and $2\,R_3SI \cdot HgI_2$ (where $R=CH_3$, C_2H_5 etc.) have been prepared (Rây and Adhikary, *J. Indian Chem. Soc.*, 1930, **7**, 297; Smiles, *J. Chem. Soc.*, 1900, **77**, 163; 1907, **91**, 1397). These are evidently complex compounds of the type $KHgI_3$ and K_2HgI_4 and should be represented as $R_3S \cdot HgI_3$ and $(R_3S)_2 \cdot HgI_4$. This has been verified by their preparation directly from R_3SI and

HgI_2 as well as by the measurements of their conductivity in acetone solutions (*cf.* Rây, *loc. cit.*).

Hydrochlor-auric acid and auric chloride react with mercaptans and sulphides leading, however, to the formation of additive compounds of the type $AuCl_3 \cdot R_2S$ and $AuCl \cdot R_2S$ (R=alkyl radicle) (Philips, *J. Amer. Chem. Soc.*, 1901, **23**, 257; Rây and Sen, *J. Indian Chem. Soc.*, 1930, 7,67). Similarly alkyl sulphides and disulphides react with silver nitrate giving rise to compounds of the type $AgNO_3 \cdot R_2S$ and $AgNO_3 \cdot R_2S_2$.

Cadmium and zinc behave like mercury and yield, when their iodides are allowed to react with alkyl sulphides or disulphides and alkyl iodides, compounds of the types $(R_3S) \cdot MI_3$ and $(R_3S)_2 \cdot MI_4$, where R_3 is either simple or mixed alkyl radicle and M is Cd or Zn (Rây, Adhikari and Banerjee—paper communicated to the Indian Chemical Society). In addition to these two types, zinc forms a compound of the type $\{(CH_3)_3S\}_4 \cdot ZnI_6$. They are in fact, strictly comparable to $KCdI_3$ and K_2CdI_4.

Antimony halides have been found to react with alkyl sulphides and alkyl halides giving a large number of compounds of the type $SbX_3 \cdot R_3SX$ or $R_3S \cdot SbX_4$, besides a compound of the type $(R_3S)_3 \cdot SbX_6$, where X=Cl, Br, or I and R=CH_3 or C_2H_5 (*cf.* Rây, Adhikari and Ray, *J. Indian Chem. Soc.*, 1931, **8**, 251). That these compounds represent true complexes of the Werner type is proved by the results of their conductivity measurements and specially by the fact that identical compounds $\{(C_2H_5)_3S\}_3 \cdot SbBr_3I_3$ is obtained when either (*i*) SbI_3 is treated with excess of $(C_2H_5)_3 \cdot S\,Br$, or (*ii*) $Sb\,Br_3$ is made to react with an excess of $(C_2H_5)_3 \cdot SI$. In the event of their being merely additive compounds, two different products, namely, $SbI_3 \cdot 3Et_3SBr$ and $SbBr_3 \cdot Et_3SI$ would have resulted. The identity of these two compounds has been established from a study of their physical and chemical properties (Rây, *loc. cit.*). The results are in perfect agreement with Atkinson's observation regarding the reactions between KCl and $SbBr_3$ on the one hand, and KBr and $SbCl_3$ on the other, the identical product $K_3(SbCl_3Br_3)$ being obtained in both cases (*Chem. News*, 1883, **47**, 175; *J. Chem. Soc.*, 1883, **43**, 291).

Antimony trichloride also reacts with alkyl sulphides yielding compounds of the type $SbCl_3 \cdot R_2S$ and $4SbCl_3 \cdot 3R_2S$, where R is an alkyl radicle. Some of these compounds, when heated in alcoholic solution, decompose and lead to the formation of compounds

of the type $2SbCl_3HCl\cdot 3R_2S$. The constitution of these compounds presents certain very interesting features. When compounds of the type, $SbCl_3\cdot R_2S$ is treated with water no oxychloride is precipitated unlike the simple antimony salts; on the other hand, the bulk of the compound is decomposed with the formation of orange antimony sulphide. Since no antimony sulphide is produced when a simple mixture of $SbCl_3$ and Et_2S is heated with water, it definitely indicates that in the compound $SbCl_3$—Et_2S the sulphur atom is directly linked to the metallic atom of antimony. The product should, therefore, be represented as a sulphonium compound of the constitution

$$\left[Cl_2Sb-S\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right]Cl$$

and be expected to behave as a strong binary electrolyte like the simple sulphonium salts. This has been strikingly verified by the conductivity and ebullioscopic measurements in acetone solution of the substance. $SbCl_3$ in acetone solution is practically a non-electrolyte, whereas the above compound in the same solution behaves as a binary electrolyte. The molecular weight of the substance in acetone, determined from the elevation of boiling point of the latter is approximately half the value calculated from its formula. This establishes, beyond doubt, the above view of its constitution.

This sulphonium nature of its constitution promises a new and very interesting line of work on the subject. If, in place of a simple sulphide like Et_2S, a mixed sulphide of the type $\begin{matrix}C_2H_5\\CH_3\end{matrix}\!\!>\!S$ be substituted, it can be easily observed that the compound formed would be resolvable into its optically active antipodes, the sulphur being asymmetrical under this condition. This is evident from the following constitutional formula

$$\left[Cl_2Sb-S\begin{matrix}CH_3\\C_2H_5\end{matrix}\right]Cl.$$

Work in this line is in progress.

With the exception of the antimony derivatives, all other above described compounds of metallic salts with organic sulphides,

when treated with dry ammonia, exchange their alkyl sulphide group with ammonia and the corresponding ammoniated metallic salts are formed. In the case of antimony compounds, however, the latter are decomposed by ammonia with the formation of antimony sulphide. This furnishes an additional evidence in favour of the sulphonium constitution of the compounds of the antimony halides with organic sulphides.

* Presidential address of the Indian Chemical Society delivered at the 7th Annual General Meeting, held in January, 1931, at Nagpur.

Kinetic Salt Effect in Methyl Alcohol Solutions. The Reaction between Sodium Bromacetate and Sodium Methoxide.

By A. N. Kappanna and H. W. Patwardhan.

Brönsted's theory of the kinetics of ionic reactions provides a method (Kappanna, *J. Indian Chem. Soc.*, 1929, **6**, 45, 419) for testing the Debye-Hückel expression for the activity coefficients of ions in dilute solutions, which is particularly useful in cases, where the activity coefficients cannot be determined otherwise. Investigations in this field have so far been confined to studies of aqueous solutions or of solutions in mixtures of alcohol and water. The present investigation relates to a pure nonaqueous solvent.

The reaction between sodium bromacetate and sodium methoxide in methyl alcohol was found by Senter and Wood (*J. Chem. Soc.*, 1915, **107**, 1070) to be bimolecular and to proceed as follows:—

$$CH_2BrCOO^- + CH_3O^- \longrightarrow CH_2(CH_3O)COO^- + Br^-.$$

The velocity was however found to increase with increasing total initial concentration. This is to be expected, as the reaction takes place between similarly charged ions. The reaction is well suited for our purpose, since throughout the reaction the ionic strength remains constant and no side-reactions occur.

The kinetics of this reaction have been studied over a wide range of ionic strengths in moderately dilute and concentrated solutions but unfortunately the work had to be discontinued. The study of more dilute solutions will be resumed as soon as circumstances permit.

EXPERIMENTAL.

C. P. methyl alcohol (free from acetone) obtained from the Mysore Iron works, Bhadravati was used. It was practically free from acetone ; only very slight traces could be detected.

To remove the traces of water, the alcohol was allowed to stand over fresh lime (well mixed) for about 24 hours and refluxed for six hours before distillation. The constant boiling middle fraction was collected and subjected to the same treatment as before. The product of this second distillation was then treated with sodium and distilled, using a long twelve bulb fractionating column. The constant boiling middle fraction was collected and stored in a big glass reservoir, darkened from outside to protect the alcohol from the action of light and fitted with a tube communicating with a phosphorus pentoxide bulb. A siphon tube enabled the alcohol to be taken out when required. Thus sodium methoxide solutions in methyl alcohol were always freshly prepared, standardised and diluted to the required extent just before use. Kahlbaum's pure monobromacetic acid, purified by recrystallisation and dried in a desiccator over phosphorus pentoxide, was dissolved in methyl alcohol when necessary in required quantities, standardised and diluted to the desired extent before use. Sodium bromacetate was formed in the reaction mixture itself by the addition of a calculated amount of sodium methoxide solution. Merck's extra pure sodium bromide, purified by recrystallisation and dried, was used.

The following procedure was adopted for studying the reaction. Adequate quantities of the reaction mixture were pipetted out at different intervals of time and mixed with known volumes of hydrochloric acid of known concentration, the quantity of the acid added being always in excess of the amount necessary for the neutralisation of the unreacted sodium methoxide. The excess of acid was titrated against, either ·1 *N*- or ·05*N*- sodium hydroxide and the quantity of sodium methoxide in the reaction mixture at the time of pipetting out computed by difference. Velocity measurements were carried out at $50° \pm 0·05°$ and $60° \pm 0·05°$ in an electrically heated and regulated thermostat.

Tables I-IV give some results of velocity measurements at 60° and are typical. Under 1 and 2 are given the equivalents of unreacted bromacetate and sodium methoxide respectively at the different time intervals in terms of c. c. of ·05 *N* solutions.

TABLE I.

Vol. titrated = 10 c.c.

Sodium methylate = 0·047 *N*; Sodium bromacetate = 0·1 *N*.

Time (min.).	1.	2.	0·434·*k*.
0	7·80	18·47	—
30	5·90	16·57	0·04029
60	4·75	15·42	0·04596
90	3·80	14·47	0·05136
150	2·60	13·27	0·04667
210	1·80	12 47	0·04519
270	1·00	11·67	0·04806
			Mean 0·04725

TABLE II.

Vol. titrated = 10 c.c.

Sodium methylate = 0·064 *N*; Sodium bromacetate = 0·0333 *N*.

Time (min.).	1.	2.	0·434·*k*.
0	12·30	6·08	—
60	10·90	4·68	0·03279
120	9 90	3·68	0·03318
180	9·15	2·93	0 03367
240	8·60	2·38	0·03378
360	7·80	1·58	0·03459
420	7·50	1·28	0·03533
			Mean 0·03388

TABLE III.

Volume titrated = 25 c.c.

Sodium methylate = 0·018 *N*; Sodium bromacetate = 0·04 *N*.

Time (min.).	1.	2.	0·494*k*.
0	8·70	19·37	—
60	7·55	18·22	0·02733
120	6·65	17 82	0·02718
180	5·80	16·47	0·02747
240	5·10	15·77	0·02784
60	4·00	14·67	0·02820
480	3 20	13·87	0·02825
			Mean 0·02771

TABLE IV.

Vol. titrated = 25 c.c.

Sodium methylate = 0·027 *N*; Sodium bromacetate = 0·012 *N*.

Time (min.).	1.	2.	0·434·*k*.
0	13·40	5·85	—
60	12·95	5·40	0·02207
180	12·15	4·60	0 02277
270	11·65	4·10	0·02298
360	11·25	3·70	0·02263
480	10·70	3·15	0·02362
			Mean 0 02281

Table V gives the results of all the experiments at 50° and 60°.

TABLE V.

Conc. of sod. bromacetate (N).	Conc. of sod. methylate (N).	Total ionic strength (μ).	0·434 $k_{50°}$.	0·434 $k_{25°}$.	$\frac{k_{50°}}{k_{25°}}$.
0·2000	0·2888	0·48880	0·09900	0 03030	3·268
0·2000	0·09328	0 29328	0·07200	0·02200	3·273
0·1000	0·04664	0·14664	0·04725	0·01420	3·327
0·0333	0·06443	0·09773	0·03388	0 01035	3·273
0·0400	0·01866	0·05866	0·02271	0·00855	3·241
0·0120	0·02710	0·03910	0·02281	0·00700	3·260
0·0060	0·01355	0·01955	0·01801	0·005894	3·271
				Mean	3·273

Figures in Table V indicate clearly that the velocity of the reaction continues to increase with increasing total ionic concentration. If A and B denote respectively the bromacetate and methylate ions and k, the bimolecular velocity constant, then according to Brönsted's theory,

$$k = \text{Constant} \cdot \frac{f_A \cdot f_B}{f_{AB}}, \qquad \ldots \quad (1)$$

where f_A, f_B and f_{AB} stand for the activity coefficients of the bromacetate, methylate and the collision complex ions respectively. A and B being of the same sign, AB will be a bivalent ion. Equation (1) can be put as

$$\log k = \log (\text{constant}) + \log \frac{f_A \cdot f_B}{f_{AB}}. \qquad \ldots \quad (2)$$

According to Debye, $-\log f_{ion} = a \cdot z^2 \cdot \sqrt{\mu}$,

where a is a constant at a definite temperature and solvent, and z, the valence of the ion. Therefore

$$-\log f_A \cdot f_B / f_{AB} = -2.a.z_A \cdot z_B \cdot \sqrt{\mu}.$$

Since $z_A = z_B = 1$, we could write $\log k = 2.a.\sqrt{\mu}$ ... (3)

This equation is applicable only to very dilute solutions. In so far as it is applicable, we should get a straight line on plotting $\log k$

against $\sqrt{\mu}$, the value of the slope being equal to $2a$. On plotting log ($0{\cdot}484\ k.a.\ 10^3$) against $\sqrt{\mu}$ (abscissae), it was found that the curve obtained was concave downwards and not a straight line. This is to be expected, as we are dealing with fairly high concentrations.

At 25°, a is equal to 2·112 for methyl alcohol and this value increases slightly with temperature, since the product of the dielectric constant and the temperature gradually diminishes with increase in temperature and a varies inversely as $(DT)^{\frac{3}{2}}$. On this basis, the slope of the curve referred to above, should have a value at least equal to about 4·80 in the ideal region and at higher concentrations this value should be expected to gradually diminish. The average value for $\frac{d \log k}{d \sqrt{\mu}}$ between 0·01955 μ and 0·05866 μ in our experiments is about 1·70, which is even less than half the value predicted by Debye-Hückel theory for the ideal region. Experimental evidence shows that strictly speaking

$$-\log f_{ion} = a.z^2 \sqrt{\mu} + \beta.c, \qquad \ldots \quad (4)$$

β has a small value in the region of concentrations used in this investigation. But it is difficult to expect that the slope of the curve between 0·0 μ and 0·02 μ to be more than double of what it is immediately above 0·020 μ. It would appear therefore that the Debye-Hückel theory does not satisfactorily explain the course of this reaction with variation in total ionic strength.

Temperature coefficient of the reaction rate.—It will be observed from the last column of Table V, that $\frac{k_{60}^{\circ}}{k_{50}^{\circ}}$ remains pretty steady throughout the range of ionic strengths examined. This is in accordance with the observation made by one of us in a previous communication (*loc.cit.*) as demanded by the Debye-Hückel expression or the Ghosh expression for the activity coefficients of ions.

It will also be noticed that the value 3·273 for the temperature coefficient of the bimolecular velocity constant in methyl alcohol is very high as compared with the usual value, 2–2·5, for the same in aqueous solutions.

Neutral salt effect.—Sodium bromide was chosen as the neutral salt, as its solubility in methyl alcohol happens to be fairly high. Table VI gives the results carried out in a definite reaction mixture,

TABLE VI.

Conc. of sodium methoxide = 0·0187M; Conc. of sodium bromacetate = 0·04N. Temp. = 60°.

Conc. of NaBr (N).	μ.	0·434 $k \times 10^3$.
0	0·0587	28·00
0·040	0·0987	32·29
0·100	0·1587	41·75
0·200	0·2587	59·23
0·400	0·4587	86·93
0·600	0·6587	112·28
0·800	0·8587	142·50

Here also the velocity gradually increases with increasing total ionic concentration. But a comparison of these figures with velocities at corresponding total ionic strengths (while total μ is made up only by the concentrations of the reacting components) shows that when sodium bromide makes up the total ionic strength, the velocities are somewhat lower. This is no doubt due to specific ionic influences, since we are dealing with moderately concentrated solutions.

Summary.

A study of the kinetics of the reaction between sodium monobromacetate and sodium methoxide in methyl alcohol has been made at 50° and 60°, at various ionic strengths over the range 0·01955μ—0·4890μ.

In accordance with Brönsted's theory, the reaction rate increases with increase in ionic strength.

For the ideal dilute region, Debye-Hückel theory predicts that $\frac{d\ log k}{d\sqrt{\mu}}$ should be equal to at least 4·3. The average experimental value for the same in the region between 0·0195μ and 0·0586μ has been found to be 1·70, which is even less than half the value predicted by theory for more dilute solutions. It is therefore inferred that even in more dilute solutions, the agreement between the experimental values and values predicted by theory may not be even approximate.

The temperature coefficient $\frac{k_{60°}}{k_{50°}}$ of the bimolecular velocity constant remains steady over the entire range of ionic strengths examined. The value 3·273 for the temperature coefficient of this bimolecular velocity constant in methyl alcohol is very high as compared with the usual value, 2−2·5 for bimolecular reactions in aqueous solutions.

The effect of adding sodium bromide in different quantities to the reaction mixture is examined over the wide range of concentrations. The velocity of reaction increases with increasing ionic strength but not so rapidly as when ionic strength is increased by the variation in the concentrations of the reactants.

CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
NAGPUR, C. P.

Received August 31, 1931.

Thixotropic Behaviour of Thorium Jellies.

By Satya Prakash and N. N. Biswas.

Prakash and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 587) and Dhar and co-workers (*ibid.*, 1929, **6**, 391 ; *ibid.*, 1930, 7, 367,417,591) have described the preparation and properties of thorium molybdate, phosphate, arsenate and other inorganic jellies. The thixotropic behaviour of thorium jellies has been dealt with in this paper.

Thorium molybdate, arsenate and phosphate jellies were obtained metathetically by mixing solutions of thorium nitrate and of the corresponding potassium salt. The jellies were allowed to set in large test tubes. The time when the tubes on inversion did not cause the overflow of the contents was noted. The 'set' jelly was vigorously shaken for about two minutes to ensure complete transformation to the sol form, and the time it took to reset was noted. The observations were repeated and the results found to be reproducible.

Thorium molybdate jelly.—To 10 c.c. of thorium nitrate solution, containing 48·24 g. of the salt per litre, were added varying amounts of 3% potassium molybdate and the total volume was made up to 15 c.c. in each case with water. On mixing the contents, a white opalescent mixture was obtained, which cleared within 3 minutes. It was allowed to stand and the setting time was noted.

Table I.

3% Potassium molybdate	Time of setting. 3 c.c.	3·5 c.c.	4 c.c.
Original setting ...	40 min.	35 min.	30 min.
After 1st. shaking ...	28	24	22
,, 2nd. ,, ...	26	20	16
,, 3rd ,, ...	26	20	16
,, 4th. ,, ...	22	20	15
,, 5th. ,, ...	22	18	15

After 5 shakings, the time of setting became practically constant. The jellies exhibited thixotropy even when allowed to age for three days, but the time of setting slightly decreased.

In the following table, 3 c.c. of 3% potassium molybdate were used in preparing the jelly.

TABLE II.

Influence of glycerol.

3 c.c. of 3% potassium molybdate.

	Time of setting.		
Glycerol	0	1·0 c.c	1·5 c.c.
Original setting ...	40 min.	85 min.	120 min.
After 1st. shaking ...	28	31	39
,, 2nd. ,, ...	26	27	27
,, 3rd. ,, ...	22	25	22
,, 4th. ,, ...	22	—	22

Glycerine stabilises the sol of thorium molybdate to a marked extent, and thus increases the original time of setting of the jelly, yet the thixotropic time finally appears to be uninfluenced by its presence.

TABLE III.

Influence of glycine.

	Time of setting.		
Glycine	0	0·5 c.c.	1·0 c.c.
Original setting ...	40 min.	50 min.	56 min.
After 1st. shaking ...	28	50	56
2nd. ...	26	19	25
3rd. ...	22	19	25
4th. ...	22	18	22

The smaller quantity of glycine decreases slightly the thixotropic time, while at higher concentrations glycine appears to behave differently. It markedly increases the original time of setting.

TABLE IV.

Influence of sucrose.

	Time of setting.		
Sucrose (20 %)	0	1·0 c.c.	2·0 c.c.
Original setting ...	40 min.	42 min.	41 min.
After 1st. shaking ...	28	27	31
2nd. ...	26	24	27
3rd. ...	22	20	25
4th. ...	22	20	25

TABLE V.

Influence of potassium sulphate.

	Time of setting.		
1·15 N—K_2SO_4	0	0·3 c.c.	0·5 c.c.
Original setting ...	40 min.	27 min.	16 min. (loose jelly)
After 1st. shaking ...	28	11	20
2nd. ...	26	11	15
3rd. ...	22	8	8
4th. ...	22	7	9

The addition of sulphate markedly decreases the time of setting. The jelly obtained is loose in structure when higher concentrations of the sulphate are used. The thixotropic time also decreases. The inconsistency observed with 0·5 c.c. of 1·15N potassium sulphate is possibly to be attributed to the weak and unsteady texture of the jelly, in its presence.

Thorium Phosphate Jelly.

Thorium phosphate jelly was prepared by the addition of varying quantities of 22 per cent. potassium phosphate (KH_2PO_4) to 10 c.c.

of the above mentioned thorium nitrate solution. As before, the total volume was fixed by dilution with water as given in the following tables. The thixotropic time is very short, being only a few seconds.

TABLE VI.

Final volume=12·5 c.c.

22 % KH_2PO_4.	Time of setting.
0·5 c.c.	70 min.
0·6	12

These jellies on shaking formed a very viscous sol, which reset within 15 seconds. With dilute jellies the thixotropic time becomes measurable (*vide* Table VII). Glycerine increases the thixotropic time.

Thorium nitrate=10 c.c. 22 % KH_2PO_4.=0·5 c.c. Total volume=15 c.c.

	Original time of setting.	Thixotropic time of setting.
No glycerine ...	1 hr. 39 min.	50 sec.
0·5 C.c. of glycerine ...	2 hrs. 15 min.	2 min.

TABLE VII.

·5 C.c. of the stock phosphate. Total volume=20 c.c.

22% KH_2PO_4=·5 c.c.

	Time of setting.	
	without glycerine	with ·5 c.c. of glycerine
Original setting ...	2 hrs. 40 min.	
After 1st. shaking ...	10 min.	3 hrs.
2nd. ...	10	43 min.
3rd. ...	10	31
4th. ...	9	21

Thus glycerine increases the original as well as the thixotropic time.

Thorium Arsenate Jelly.

Different concentrations of 18 per cent. potassium arsenate solution were used and the total volume was made up to 12·5 c.c. In the beginning, the mixture is opalescent but clears up in a few minutes. It again develops opalescence, becomes translucent when it has set. In contrast to the others, on further standing, the opalescence increases and the solution may finally become opaque.

As soon as the jelly set originally, it was shaken for about a minute and the opalescent sol thus obtained was again allowed to set and the process was repeated, till a perfectly opaque jelly was obtained which broke on the further shaking (Table VIII).

TABLE VIII.

	Time of setting.		
18 % KH_2AsO_4	1·0 c.c.	1·1 c.c.	1·2 c.c.
Original setting ...	53 min.	42 min.	63 min. (non-homogeneous jelly)
After 1st. shaking ...	7	8	11
2nd. ...	3	6	6
3rd. ...	2½	5	5
4th. ...	2	4	4
5th. ...	2	2	breaks
6th. ...	breaks	breaks	—

TABLE IX.

Influence of glycerine.

18% KH_2ASO_4=1·1 c.c.

	Time of setting.	
Glycerine ...	0	0·5 c.c.
Original setting ...	42 min.	82 min.
After 1st. shaking ...	8	7
2nd. ...	6	4
rd. ...	5	3
4th. ...	4	breaks

Glycerol has got a peptising and stabilising influence on the thorium arsenate sol, but does not enhance the thixotropic time. Possibly glycerine by increasing the time of the original setting helps the ageing of jelly forming elements.

Discussion.

The results recorded in the previous tables show that the thorium molybdate and phosphate jellies are highly thixotropic. Thorium arsenate jellies which develop slight opalescence on ageing exhibit this property only when freshly formed, but afterwards they break up when shaken. The velocity of sol-gel transformation in the case of phosphate jellies is very great, so much so, that in some cases it is almost instantaneous. However, if the jellies are diluted, the transformation proceeds at a measurable speed. In all these cases, the original time of setting is much greater than the thixotropic time.

In previous publications (*loc. cit.*), it has been stated that the formation of jellies is guided by two tendencies of the uncharged particles. When the charge on the colloidal particles is decreased by the adsorption of oppositely charged ions from the electrolytes, the particles tend to agglomerate, and in the case of hydrophilic sols, they simultaneously develop hydration. Where the hydration tendency is most marked, the transparent jellies like thorium molybdate and phosphate are formed, but in cases where the agglomeration tendency is also marked, the opalescent jellies, as in the case of thorium arsenate, are obtained. It appears that with the increase in the agglomeration tendency, the thixotropy decreases and such jellies are liable to break up on shaking.

We have also shown that as the concentration of coagulating electrolytes, that is that of the oppositely charged ions is increased, the jelly forming particles tend to develop more agglomeration, which is exhibited either in the form of the shrinkage of the jelly-forming network, when the phenomenon of syneresis is exhibited or in the development of opalescence. In this communication, we have shown from our results on the influence of potassium sulphate, that with the increase of its concentration, the thixotropic property of the jelly is also decreased. When the higher concentrations of this substance are used, the jelly breaks up on shaking. We are of the opinion that for these reasons, the opaque jellies or the jellies undergoing syneresis will not exhibit thixotropy.

According to von Weimarn (*Rep. Imp. Ind. Res. Inst., Osaka*, 1928, 9, 1), the total amount of water imbibed in a jelly is supposed to consist of (*i*) interatomic hydration *e.g.*, the water in crystal hydrates, (*ii*) 'surface hydration', *i.e.*, the water adsorbed on the surface of the uncharged particles, and (*iii*) 'structure hydration' *i.e.*, water enclosed by the pores of the structural elements of the jelly. It appears that along with other factors, the extent of thixotropy depends upon this structurally imbibed liquid. The shaking of a jelly does not markedly influence the surface hydration, while the structurally imbibed liquid is set free when the jelly is agitated. The thixotropic time appears to be the time taken by the sol, so formed, to resume the former structure of the jelly. It has been observed that the original setting time is by far greater than the thixotropic time. This is easily explained, because the original setting time was the time taken by the jelly forming particles to develop surface hydration on slow neutralisation of the charge and also to develop structure hydration; and it must be greater than the thixotropic time where only the structure is redeveloped. This is also clear from the fact that the thixotropic time for a dilute thorium phosphate jelly is greater than for the concentrated one, because in the case of a dilute jelly, the water would be more structurally imbibed.

From the results obtained in this paper, it would be seen that glycerine, glycocoll and to a slight extent sucrose also, act as stabilising agents, while potassium sulphate increases the velocity of the gel formation. Glycerine and sucrose are really peptising agents. They possibly influence the preferential adsorption capacity for various ions. The action of glycocoll is amphoteric. In small concentrations, it slightly decreases the thixotropic time. This is due to the diminution of hydrogen ions in its presence. Freundlich (*Kolloid Z.*, 1928, **45**, 348) has also observed that the addition of aminoacids to the ferric oxide sols lowers the hydrogen-ion concentration. But with ferric oxide sols, he observed that glycine has got a stabilising influence, and this he ascribed to the tendency of aminoacids to form complex ferric salts. At higher concentration of glycine, we have also observed that its sensitising influence is markedly decreased. It is probable that such anomalies in the case of glycine are due to its amphoteric nature, and not to complex formation.

The phenomenon of thixotropy does not support the view that

the jellies are formed by the release of supersaturation, as has been advanced by von Weimarn. In fact, the solid masses, however transparent they may be, formed by the release of supersaturation (as the jellies of barium sulphate) cannot be retransformed into the solid state by shaking and cannot slowly build up the structure again.

Summary.

1. Thixotropy has been studied in the case of thorium molybdate, phosphate and arsenate jellies. Molybdate and phosphate jellies are highly thixotropic, while opalescent arsenate jellies are only thixotropic when freshly formed; afterwards they lose this property and break up on shaking.

2. The original time of setting of a jelly has been found to be much greater than the thixotropic time of setting. The thixotropic time attains almost a constant value, if the agglomeration tendency is not markedly developed, while it continuously decreases in the case of the agglomerated jellies as thorium arsenate.

3. The thixotropic time in the case of diluted jellies is greater than in the case of concentrated jellies, because, in the former case, the jelly consists of a larger quantity of structurally imbibed liquid.

4. Thixotropy has been explained on the view of the authors' 'hydration-agglomeration hypothesis of jellies'. On shaking, the structurally imbibed liquid of a jelly is set free forming a dispersion medium for the jelly-forming elements, and thus the thixotropic jellies are transformed to the sol condition. The structure is again developed and the gel is again formed.

5. Glycerol and sugar act as peptising agents and in their presence, the original setting time, as well as the thixotropic time, are increased. Glycocoll acts as an amphoteric substance. In small quantities, it decreases the thixotropic time on account of the diminution of hydrogen-ion concentrations. At higher concentrations, it has got a slight stabilising influence. Addition of potassium sulphate decreases the time of original, as well as, thixotropic setting.

6. The phenomenon of thixotropy cannot be explained on the view that the jellies are formed by the release of highly developed supersaturation, as is thought by von Weimarn.

CHEMICAL LABORATORIES,
UNIVERSITY OF ALLAHABAD,
ALLAHABAD.

Received August 6, 1931.

A Study of the Kinetics of the Inversion Process in Dilute Solutions of Sucrose in Presence of Hydrochloric Acid.

By A. N. Kappanna and J. G. Shrikhande.

Studies on the kinetics of the inversion of sucrose have generally been made with fairly concentrated solutions (generally with ten per cent. and more and in a few cases with five per cent. solutions). The investigations of Lewis and collaborators (*J. Chem. Soc.*, 1920, **117**, 1120; *ibid.*, 1922, **121**, 1613) and Scatchard (*J. Amer. Chem. Soc.*, 1921, **43**, 2387; *ibid.*, 1923, **45**, 1580) show that the mechanism of the inversion process is a highly complicated one and the presence of large amounts of cane sugar in the reaction mixtures increases the complexities of the problem. It occurred to us that a study of the course of inversion in very dilute solutions of sucrose might lead to a better understanding of the problem and the present investigation was accordingly undertaken.

We have adopted a purely chemical method for the estimation of invert sugar in the reaction mixture.

Experimental.

All the chemicals employed in the present investigation were of the highest grade purity, either Merck's or Kahlbaum's guaranteed analytical reagents. The specimen of cane sugar used was Merck's preparation for the determination of heat of combustion. The purity of this was tested polarimetrically before use and found perfectly satisfactory.

Most of the velocity measurements were carried out at $35° \pm 0·05°$ and a few at $45° \pm 0·05°$, in an electrically regulated thermostat.

Conductivity water from a Hartley's still was used for the preparation of all the solutions.

Estimation of invert sugar.—It is well known that the amount of sucrose present along with reducing sugars greatly influences the extent to which Fehling's solution is reduced, thus introducing error in the estimation of any reducing sugar. It is also known that no

such error creeps in, if the total amount of sugar (reducing sugar + sucrose) taken for each assay does not exceed 100 milligrams (Quisumbing and Thomas, *J. Amer. Chem. Soc.*, 1921, **43**, 1521).

We have adopted in this investigation, for the estimation of invert sugar, a modification of the method of Brown, Morris and Millar (*J. Chem. Soc.*, 1897, **71**, 281).

The Fehling's solution was prepared according to the formula of Ling and Rendle (*Analyst*, 1908, **33**, 167) and had the following composition:—

Solution I—69·28 g. of copper sulphate pentahydrate per litre.

Solution II—346 g. of Rochelle salt
142 g. of caustic soda } per litre.

(In solution II, Brown and co-workers used only 130 g. of caustic soda).

The two solutions were kept separate and the required quantities of the mixture prepared just before use.

Procedure.—A definite amount of the reaction mixture containing not more than 100 milligrams of total sugar was pipetted out into an Erlenmeyer flask containing an amount of alkali just enough to neutralise the catalysing acid. This was then mixed with 50 c.c. of Fehling's solution, the mouth of the flask covered with a small beaker and heated in a water-bath at 99°-100° for exactly 12 minutes.

Brown, Morris and Millar recommend heating Fehling's solution only in boiling water first and then, after adding the sugar solution, heating the mixture in the bath for exactly 12 minutes. We have found, however, that when we use the Fehling's solution prepared to Ling's formula, quantitative results are obtained by heating the mixture for exactly 12 minutes in the water-bath.

The mixture after reaction was rapidly filtered through asbestos in a Gooch crucible, the entire cuprous oxide precipitate transferred to the crucible and well washed with distilled water, free from air and carbon dioxide. Next the asbestos mat with the cuprous oxide precipitate was transferred back to the Erlenmeyer flask. The crucible was then placed in a funnel over the flask and carefully rinsed first with 25 c.c. of a saturated solution of ferric alum in 25 p. c. sulphuric acid and then with 25 c.c. of 25 p. c. sulphuric acid, so that any

precipitate sticking to the sides of the crucible might get dissolved and the entire washings collected in the flask. A pinch of sodium carbonate was next added to the flask, the mouth of the flask closed with a rubber cork and the flask gently shaken. The entire precipitate dissolved in less than a minute. The mixture was then titrated against standard decinormal permanganate solution; (Brown and coworkers estimate the cuprous oxide gravimetrically). The amount of permanganate solution required for the titration is a measure of the amount of invert sugar present and the amount of unhydrolysed sucrose is computed by difference. The method gives accurate results, the error being generally between 0·40 and 0·50 per cent.

Results and Discussion.

The results of two characteristic experiments are given in Tables I and II.

TABLE I.

Temp.=35°. Conc. of sucrose=1·0 p.c. Conc. of HCl=0·10 *N*. 10 C.c. taken for each analysis.

Time (min.).	Amount of sucrose in 10 c.c. (mg.).		0·434 *k*.
0	89·00		—
30	80·50		0·001458
60	72·67		0·001468
90	65·83		0·001455
120	59·50		0·001458
150	53·50		0·001466
210	43·67		0·001472
270	36·17		0·001449
330	29·50		0·001453
390	23·00		0·001471
∞	0·00	Mean	0·001460

TABLE II.

Temp.=35°. Conc. of sucrose=0·10 p.c. Conc. of HCl=0·10*N*. 50 C.c. taken for each analysis.

Time (min.).	Amount of sucrose in 50 c.c. (mg.).		0·434 *k*.
0	42·83		—
30	38·87		0·001420
60	35·17		0·001425
90	32·00		0·001407
120	29·17		0·001411
150	26·17		0·001426
210	21·67		0·001409
270	17·67		0·001424
330	12·00		0·001416
∞	0·00	Mean	0·001417

Table III contains data obtained with different concentrations of sucrose, at 35° and 45°, the concentration of hydrochloric acid being the same (0·10 %) in all the solutions.

TABLE III.

Conc. of sucrose (M).	0·434 $k_{35°}$.	0·434 $k_{45°}$.	$k_{45°}/k_{35°}$.
0·002924	0·001417	0·004969	3·506
0·007310	0·001430	0·005000	3·496
0·01462	0·001441	0 005058	3·510
0·00924	0·001460	0·005111	3·500
0·05848	0·001477	0·005171	3·501
0·03772	0·001478	0·005193	3·513
0·1462	0·001482	0·005203	3·511
0·2924	0·001522	0·005333	3·504
		Mean	3.505

Comparison of the values of the velocity constants with those obtained by the polarimetric method.—Moran and Lewis (*J. Chem. Soc.*, 1922, **121**, 1617) find for the velocity constant with a 10 per cent. sucrose solution and 0·10 N hydrochloric acid at 35° a value $k=5·65\times10^{-5}$ (calculations made to the base e and seconds^{-1}). Under the same conditions we find from the results given in Table III that $k=5·83\times10^{-5}$. By extrapolation, Lewis and Moran obtain for zero concentration sucrose $k=5·00\times10^{-5}$, while in our experiment with 0·10 per cent. sucrose solution, we find $k=5·432\times10^{-5}$. The agreement between the values of k in the case of 10 per cent. sucrose solution is quite satisfactory, while in the case of solutions, whose sucrose concentration is in the neighbourhood of zero, the difference is about 8 per cent. It may therefore be concluded that the chemical method gives almost the same results as the polarimetric method.

Variation of k with concentration of sucrose.—A glance at Table III shows that with increase in the concentration of sucrose from 0·10 per cent. to 10 per cent. at constant catalyst concentration, the velocity constant gradually, though slowly, increases at constant temperature. It has been shown by Moran and Lewis (*J. Chem. Soc.*, 1922, **121**, 1620) that the activity of the hydrogen ion in decinormal solutions of hydrochloric acid increases with increase in sucrose concentration and the activity of the hydrogen ion certainly exerts the major regulating effect on the velocity of hydrolysis. If k varies directly as the activity of the hydrogen ion, then $\frac{k_{10\%}}{k_{0·10\%}}$ must be equal to $\frac{a_{H^+10\%}}{a_{H^+0·10\%}}$ where $a_{H^+10\%}$ and $a_{H^+0·1\%}$ represent the activities of the hydrogen ions in 10 per cent. and 0·10 per cent. solutions of sucrose respectively. If we assume

that a 0·10 per cent. solution of sucrose approximates in its properties to pure water, according to Moran and Lewis (*loc. cit.*) $\left(\frac{a_{H^+}10\%}{a_{H^+}\text{pure water}}\right)$ is equal to 1·192 while according to our experiments $\frac{k_{10\%}}{k_{0\cdot10\%}}$ is equal to 1·074. This means that the rate of increase of velocity is not as great as the rate of increase of activity of the hydrogen ion.

Temperature coefficient of k.—Figures in the extreme right column of Table III indicate that $\frac{k_{45^\circ}}{k_{35^\circ}}$ is quite constant over the entire range of concentrations of sucrose studied, the average value for this ratio being 3·505. This gives on calculation 24541 calories as the energy for the critical increment, while the results of Moran and Lewis (*loc. cit.*) lead to the value 26105 calories for the same.

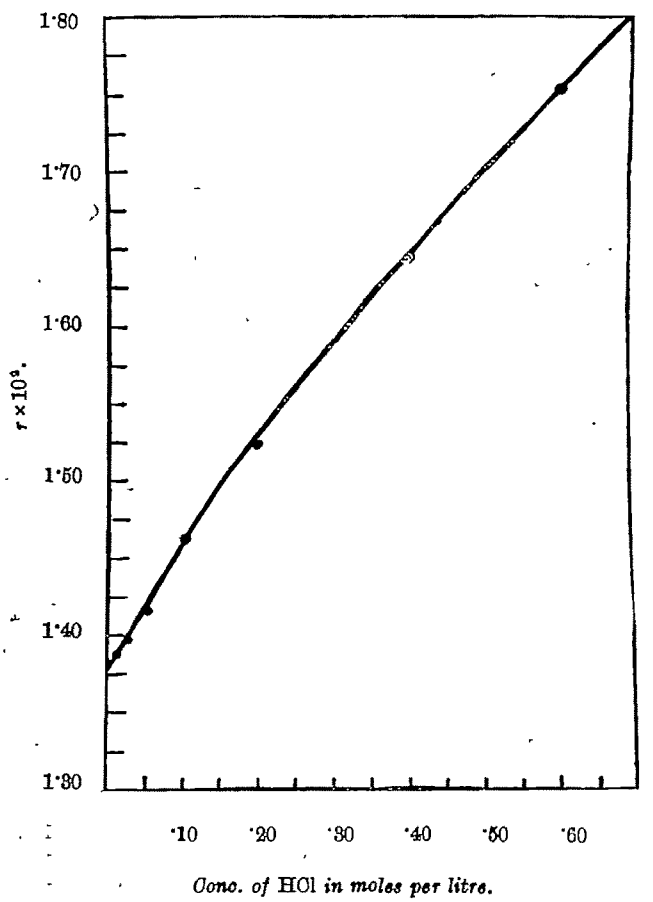
Variation of k with acid concentration.—Table IV summarises the results at 35° obtained with different concentrations of hydrochloric acid. In all these experiments, the concentration of sucrose was the same (1 g. per 100 c.c.). In the third column of the table are given values for the ratio $\frac{0\cdot434\ k\times10^2}{C_{HCl}}=r$, in the fourth column the activities of hydrogen ions in the different solutions and in the fifth column values for the ratio $\frac{0\cdot434\ k\times10^2}{a_{H^+}}$.

TABLE IV.

Conc. of HCl (mole/litre).	$0\cdot434\ k\times10^4$.	r.	a_{H^+}.	$\frac{0\cdot434\ k}{a_{H^+}}\times10^4$.
0·001	1·877	1·877	0·000993	1·886
0·002	2·758	1·379	0·001972	1·400
0·005	6·895	1·379	0·004835	1·426
0·008	11·050	1·381	—	—
0·010	18·850	1·885	0·00933	1·489
0·020	27·840	1·392	0·01850	1·508
0·050	70·750	1·415	0·04420	1·578
0·100	146·000	1·460	0·08660	1·683
0·200	304·000	1·520	0·1714	1·773
0·400	655·200	1·638	0·3572	1·834
0·600	1050·600	1·751	0·5748	1·828
0·800	1508·800	1·886	0·8336	1·809
1·000	2010·000	2·010	0·1410	1·761

These figures show that in very dilute solutions (up to about 0·01 *N*) of the acid, *r* remains almost constant and then it begins to increase with increased concentration of the acid. *r* plotted against the concentration of the acid (*c* as abscissae) gives a curve which is slightly concave downward (Fig. 1). This means

FIG. 1.



that the salt effect of the acid molecule is greater at lower than at higher concentrations.

The ratio $\frac{k}{C_{HCl}}$ is to be regarded as the molar velocity constant in this catalysis. If $\frac{k}{C_{HCl}} = V$, then $r = 0{\cdot}434\ V$. From the curve in Fig. 1 we get the following relation

$$0{\cdot}434V = 1{\cdot}376 \times 10^{-2} + 0{\cdot}84 \times 10^{-2} \cdot C_{HCl},$$

for the molar velocity constant for concentrations of acid up to about $0{\cdot}12N$.

Activity of the hydrogen ion and the velocity constant.—Since the concentration of sugar in the above experiments is very small, we might assume that the influence of sucrose in these solutions on the activities of H^+ and water is negligible. The measurements of Harned (*J. Amer. Chem. Soc.*, 1920, **42**, 1808) furnish us with data regarding the activity coefficients of H^+ in solutions of HCl of different concentrations at 25°. The activity coefficient of an ion does not vary very much over a small range of temperature like 10° and we might regard the activities of H^+ in different solutions at 35° to be the same as at 25°. The values given in Harned's paper refer to molal concentrations of hydrochloric acid. For our purposes we have calculated the corresponding values for molar concentrations from Harned's data and these are the values given in column of 4 Table IV.

It will be observed from the table that even in very dilute solutions of the acid the ratio $\frac{0{\cdot}434\ k}{a_{H^+}}$ very rapidly increases with increased concentration of the acid. If the activity of the catalysing ion is what tells in the reaction, we should have found the ratio $\frac{0{\cdot}434\ k}{a_{H^+}}$ constant at different concentrations of the acid, at least in very dilute solutions. It is to be particularly noted that the values for the ratio $\frac{0{\cdot}434\ k}{a_{H^+}}$ are always higher than $\frac{0{\cdot}434\ k}{C_{HCl}}$ at corresponding concentrations of the acid, except at the last two concentrations of the acid studied. This shows that the velocity constant increases much faster than is warranted by the increase in the thermodynamic concentration of hydrogen ion.

Effect of neutral salts.—Table V gives the results of velocity of measurements made to test the influence of neutral salts. In these experiments, the concentrations of sugar and hydrochloric acid were kept constant (1 g. of sucrose per 100 c.c. and 0·10 *N*-HCl) while the concentrations of the salts were varied. Experiments were carried out only with the chlorides of potassium, sodium and lithium.

TABLE V.

0·484 $k \cdot 10^4$.

Salt Conc. (mole/litre).	KCl.	NaCl.	LiCl.
0	14·60	14·60	14·60
0·10	15·30	15·30	15·40
0·20	15·70	15·88	16·27
0·50	17·00	17·80	18·10
1·00	19·59	20·91	22·80
2·00	27·23	29·12	33·50
3·00	37·35	43·80	49·83

Results given in Table V indicate that the effectiveness in increasing the velocity constant for the three salts investigated is in the following order—LiCl > NaCl > KCl.

Very recently Kautz and Robinson (*J. Amer. Chem. Soc.*, 1928, **50**, 1022) have made a study of the hydrolysis of sucrose with hydrochloric acid, in presence of alkali and alkaline earth chlorides at 25°. Their results were obtained with 20 per cent. sugar solutions. The concentrations of salts and hydrochloric acid employed by them were the same as in our experiments. Our experiments were of course carried out at 35°. In Table VI we have compared the ratios we obtain from our results $\frac{k \text{ (velocity constant in presence of salt)}}{k_0 \text{ (velocity constant only with } 0 \cdot 10N\text{-HCl)}}$ with the corresponding ratios taken from Kautz and Robinson's paper. Figures given under the subscripts (K&S) and (K&R) refer to our and Kautz and Robinson's results respectively.

TABLE VI.

Salt conc. (mole/litre).	k/k_o (K&R)	k/k_o (K&S)	k/k_o (K&R)	k/k_o (K&S)	k/k_o (K&R)	k/k_o (K&S)
	KCl		NaCl		LiCl	
0·10	1·07	1·048	1·13	1·048	1·14	1·054
0·20	1·15	1·075	1·18	1·088	1·21	1·114
0·50	1·26	1·164	1·27	1·185	1·30	1·239
1·00	1·51	1·341	1·54	1·432	1·57	1·527
2·00	2·24	1·865	2·26	1·994	2·52	2·294
3·00	3·12	2·548	3·47	2·965	4·07	3·413

It will be observed that the ratios obtained by us are throughout lower (very much lower at higher concentrations of salts) than the corresponding ratios obtained by Kautz and Robinson. As pointed out above, their results were obtained with 20% sugar solutions. Since, in general, the activities of ions are much greater in sugar solutions than in pure water, assuming that our dilute sugar solutions approximate in behaviour to pure water, we can qualitatively explain the higher values obtained by Kautz and Robinson, as being due to the higher activites of hydrogen ions in the solutions employed by them.

It is worthwhile examining how far our results can be accounted for by the increased activity of hydrogen ions in salt solutions. Harned(*loc. cit.*) has determined by *E. M. F.* measurements the activity coefficients of hydrogen ion in decinormal solutions of hydrochloric acid in the presence of alkali chlorides at 25°. If we were to assume here again, that the activity coefficient of an ion at 35° does not differ much from its value at 25° in any given solution, we could utilise Harned's data for our present purpose. If the velocity constant of the reaction is strictly proportional to the activity of the hydrogen ion, we ought to get a constant value for the ratio $\frac{0{\cdot}434.\ k}{a_{H^+}}$. These ratios in the different solutions together with the activities of hydrogen ions in those solutions are given in Table VII.

TABLE VII.

Salt conc.	KCl		NaCl		LiCl	
(M).	a_{H^+}.	$0{\cdot}434k/a_{H^+}$.	a_{H^+}.	$0{\cdot}434k/a_{H^+}$.	a_{H^+}.	$0{\cdot}434k/a_{H^+}$.
0·0	0·0869	1·680				
0·10	0·0876	1·747	0.0897	1·706	0·0908	1·698
0·20	0·0884	1·776	0·0918	1·780	0·0945	1·722
0·50	0·0929	1·880	0·0989	1·749	0·1066	1·698
1·00	0·1018	1·925	0·1152	1·815	0·1362	1·638
2·00	0·1926	2·054	0·1681	1·733	0·2290	1·464
3·00	0.1785	2·093	0·2660	1·618	0·4100	1·215

It will be seen from Table VII, that the ratio $0{\cdot}434k/a_{H^+}$ is in no case constant. In the case of potassium chloride, it gradually increases with increased concentration of salt. In the case of sodium chloride, it reaches a maximum at 1·0 N and then falls, while in case of lithium chloride solutions, the maximum is reached even at 0·20 N and then it begins to fall. The increase in velocity constant would therefore appear to be more subject to the specific influences of the different salts and cannot be attributed merely to the hydrogen ion activities in the salt solutions.

Schmid and Olsen (*Z. Phys. Chem.*, 1926, **97**, 124) proposed the following empirical relation between the molar concentration of the salt and the velocity constant, $k=k_0e^{ac}$, where k_0 is the velocity constant in the absence of salt, c the concentration of the added salt and a a constant for any particular salt. Grube and Schmid (*Z. Phys. Chem.*, 1926, **119**, 19) have found this simple relationship to hold good also in the case of the acid hydrolysis of cyanamide. This expression can be written in the form $\log k=\log k_0+a.c.$

We find plotting log ($0{\cdot}434\,k$) from our data against c, that very good straight lines are obtained in the case of all the three salts, as demanded by the above expression. For the three salts KCl, NaCl and LiCl, the characteristic constants have values 0·135, 0·1564 and 0·1767 respectively.

Considerations regarding the mechanism of the reaction.—Scatchard (*J. Amer. Chem. Soc.*, 1921, **43**, 2387) drew attention to the fact that previous workers, who tried to interpret data on the kinetics of sucrose hydrolysis, did not practically take into account

the role water played in the reaction. In his two papers on the mechanism of the inversion process in concentrated sucrose solutions (*loc. cit.*), he started with the assumption that n molecules of water take part in the reaction and introducing this factor into the kinetic expression, arrived at the equation

$$k = \frac{k_{uni}}{a_{H^+} \times a_w^n},$$

where k_{uni} stands for the usual unimolecular velocity constant, a_{H^+}, the activity of the hydrogen ion and a_w, the activity of water. Scatchard finds that when n is assigned a value of 6, the observed results could be quantitatively explained. We tried to apply this equation and see how far the data in Tables IV and V of this paper lend support to this mechanism. We calculated the activities of water in different HCl and salt solutions from the best available vapour pressure data and found that in no case could we get constant values for k in the above equation. With increased electrolyte concentration, we found that the value for the ratio $\frac{k_{uni}}{a_{H^+} \times a_w^6}$ gradually increased. We have therefore not given the results of these calculations here.

It is clear from what we have seen in previous sections of the paper, that the velocity of hydrolysis, even in very dilute solutions of sucrose, does not vary simply as the activity of the hydrion. It is now generally recognised that hydrogen ion in water exists not as mere proton but as the hydrated ion H_3O^+(Brönsted, Acid and Basic Catalysis, Chemical Reviews, V. 1928. Chapters VI, VII and VIII.). It is possible that the hydrolysis is a mere bimolecular reaction taking place between the sucrose (S) and the oxoniun ion, according to the scheme

$$S + H_3O^+ \longrightarrow \text{Glucose} + \text{Fructose} + H^+ \text{ (measurable)};$$

followed by

$$H^+ + H_2O \longrightarrow H_3O^+ \text{ (instantaneous)}.$$

According to this scheme, the expression for the reaction rate according to Brönsted's theory will be

$$k = k_1 . C_s . C_{H_3O} . \frac{F_s . F_{H_3O^+}}{F_x^+} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where F_s, $F_{H_3O^+}$ and Fx^+ stand for the activity coefficients of the sugar molecule, H_3O^+ ion and the critical collision complex respectively. In very dilute solutions, the activity coefficients of all univalent ions may be regarded as being equal and the activity coefficient of the nonelectrolyte sucrose molecule as being equal to unity, so that we should expect the above expression (1) to assume the simple classical form

$$h = k_1 . C_s . C_{H_3O^+}.$$

Since during the course of the reaction $C_{H_3O^+}$ remains constant,

$$h = k . C_s,$$

where k is the unimolecular velocity constant, being equal to $k_1 . C_{H_3O^+}$. It follows therefore

$$k_1 = k/C_{H_3O^+} \quad \ldots\ldots\ldots\ldots \quad (2)$$

We find actually from Table IV that this relationship holds good only for very dilute solution up to a concentration of hydrochloric acid 0·008 *N*.

It should however, be pointed out here that above conclusion can be arrived at for very dilute solutions, even if it be assumed, as has been done by Scatchard (*loc. cit.*), that water molecules also take a direct part in the reaction.

For more concentrated solutions, this relationship cannot be expected to hold good. $F_{H_3O^+}$ and F_{x^+} should be expected to have different values, specific individual effects coming into prominence. If, however, the ratio $F_{H_3O^+}/F_{x^+}$ does not considerably deviate from unity, then also we should expect to get constant values for $F_{H_3O^+}$. But there is yet F_s, whose value ought to vary with increase in concentration of electrolytes. The variation of F_s with concentration of electrolytes is not exactly known and there is no way of determining F_{x^+} at different ionic concentrations, so that these difficulties stand in the way of testing any hypothesis regarding the mechanism of this reaction in a quantitative way.

Summary.

A study of the hydrolysis of sucrose in presence of hydrochloric acid has been made under the following conditions:—

(1) With different concentrations of cane sugar in the range 0·002924*M*—0·2924*M*, keeping the concentration of hydrochloric acid constant (0·10*N*) at 35° and 45°.

(2) With different concentrations of hydrochloric acid in the range $0{\cdot}001N-1{\cdot}00N$, keeping the concentrations of cane sugar constant ($0{\cdot}02924M$) at 35°.

(3) With different concentrations of the three neutral salts KCl, NaCl and LiCl in the range $0{\cdot}10N-3{\cdot}0N$, keeping the concentrations of sucrose ($0{\cdot}02924$ M) and hydrochloric acid ($0{\cdot}10$ N) constant at 35°.

It has been found that under the conditions specified in (1) with increase in sucrose concentration at constant temperature, the velocity constant gradually increases, but the rate of increase is not as great as the rate of increase of the activity of hydrogen ion in these solutions.

$k_{45°}/k_{35°}$ is quite constant over the entire range of concentrations of sucrose, having an average value 3·505.

Under the conditions specified in (2), the ratio k/C_{acid} remains constant in dilute solutions up to a concentration of about $0{\cdot}01N$ and then increases with increase in concentration of acid. The molar velocity constant V, in this catalysis, up to a concentration of about $0{\cdot}12N$ has been found to be faithfully expressed by the equation

$$0{\cdot}434V = 1{\cdot}376 \times 10^{-2} + 0{\cdot}84 \times 10^{-2}.C,$$

where C is the concentration of the acid.

The neutral salt effect in the reaction has been found to follow the simple empirical relation, $k = k_0 e^{ac}$, proposed by Schmid and Grube (*Z. Phys. Chem.*, 1926, **119**, 19) and Schmid and Olsen (*Z. Phys. Chem.*, 1926, **124**, 97). The characteristic constant (a) for the three salts KCl, NaCl and LiCl have been found to be equal to 0·135, 0·1564 and 0·1767 respectively.

In the presence of salts, the increase in hydrogen ion activity does not account quantitatively for the increase in velocity of hydrolysis.

A few points regarding the mechanism of the hydrolysis have been briefly discussed.

We wish to express our gratitude to the Government of Central Provinces in the Minstry of Education, for the award of a research fellowship to one of us (J.G.S) which enabled him to take part in this investigation.

CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
NAGPUR, C. P.

Received July 17, 1931.

Studies in Quinoline Compounds. Part V.

By Upendra Nath Brahmachari and Tarapada Bhattacharjee.

In our previous communications we prepared the simple substitution products of 8-aminoquinolines. The present paper deals with certain amino*iso*propyl derivatives of 8-aminoquinolines. The characteristic feature of these compounds is that there is an assymetric carbon atom in the side-chain which is also a speciality of plasmochin. In short, these compounds can be looked upon as the lower homologues of plasmochin which, as it is understood, is an amino*iso*pentyl derivative of 8-aminoquinoline.

In the successive condensation of β-bromopropylphthalimide which was obtained in good yield by a modification of Seitz's method (*Ber.*, 1891, **24**, 2624), with 8-aminoquinoline or its derivatives, we have followed the method of Baldwin (*J. Chem. Soc.*, 1929, p. 2962). In this case the time for condensing the β-bromopropylphthalimide was considerable, in some cases nearly 24 hours being needed for the completion of the reaction. The successive action of hydrazine in boiling alcoholic solution and hydrochloric acid on the resulting 8-β-phthalamido*iso*propylaminoquinolines, effected, as was found by Baldwin, a smooth hydrolysis and the dihydrochlorides of compounds of the nature of 8-β-amino*iso*propylaminoquinoline were easily isolated. In this way we have prepared the following compounds:

(1) 8-β-Amino*iso*propylaminoquinoline.
(2) 8-β-Amino*iso*propylamino-6-methylquinoline.
(3) 8-β-Amino*iso*propylamino-6-methoxyquinoline.
(4) 8-β-Amino*iso*propylamino-6-ethoxyquinoline.

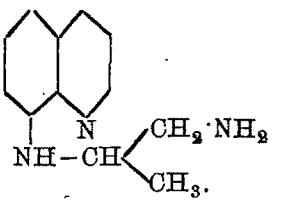
The free bases are generally uncrystallisable and therefore we have not isolated them. The bihydrochlorides are solids which can be easily crystallised from absolute alcohol. These dissolve very easily in water giving rise to a faintly acidic solution. The alkylation of these compounds is not very difficult, but the products cannot be obtained in a very pure state.

For the sake of comparison we have also prepared the (1) 8-β-aminoethylaminoquinoline, (2) 8-β-aminopropylaminoquinoline.

We would point out here that the condensation of β-bromopropylphthalimide can only be effected with 8-aminoquinoline and its derivatives, whereas the isomeric 6-, 7-, or 5-aminoquinolines cannot be made to undergo this condensation.

Experimental.

8-β-Aminoisopropylaminoquinoline,



The starting materials are β-bromopropylphthalimide and 8-aminoquinoline, of which the former is prepared by heating allylphthalimide (6 g.) with fuming hydrobromic acid (*d* 1·78, 10 c.c.) for about 10 minutes on a boiling water-bath and then pouring into water. The solid thus separated is then crystallised from dilute alcohol, m.p. 150°.

β-Bromopropylphthalimide (5 g.) is intimately mixed with 8-aminoquinoline (3 g.) and heated on an oil-bath at 125-35° for about 24 hours, when the separation of the solid hydrobromide is nearly complete. The nearly solid mixture is then stirred up with absolute alcohol and filtered. The precipitate is washed thoroughly with alcohol and dried in vacuum, yield 4 g.

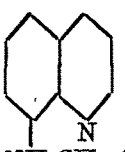
The above hydrobromide (4 g.) is suspended in absolute alcohol (25 c.c.) and 1·5 c.c. (2·5 mols.) of hydrazine hydrate added into it. The mixture is heated on the water-bath for 1½ to 2 hours. The alcohol is then driven off and the white spongy residue is mixed with an excess of 2*N*-hydrochloric acid and heated on a boiling water-bath for 15 minutes. The precipitated phthalylhydrazide is filtered off and the filtrate basified. The base is taken up with chloroform. On passing dry hydrogen chloride into the dry chloroform solution, the bihydrochloride is precipitated, and is recrystallised from absolute alcohol. It is a brownish yellow solid, easily soluble in water, m.p. 285°. The solution is only faintly acidic. (Found: N, 15·5. $C_{12}H_{17}N_3Cl_2$ requires N, 15·3 per cent.).

8-*β-Amino*isopropylamino-6-*methylquinoline*.—The preparation of this compound is almost the same as the previous one. The separation of the intermediate hydrobromide is nearly complete within 12 hours. The bihydrochloride is a brownish yellow solid melting at 255°. It is very easily soluble in water, moderately soluble in absolute alcohol from which it is recrystallised. (Found: N, 14·8. $C_{13}H_{19}N_3Cl_2$ requires N, 14·6 per cent.).

8-*β-Amino*isopropylamino-6-*methoxyquinoline* is prepared from β-bromopropylphthalimide (4 g.) and 6-methoxy-8-aminoquinoline (2·5 g.). It is a yellow solid melting at 221°. (Found: N, 13·7. $C_{13}H_{19}ON_3Cl_2$ requires N, 13·8 per cent.).

8-*β-Amino*isopropylamino-6-*ethoxyquinoline* melts at 231° (Found: N, 13·0. $C_{14}H_{21}ON_3Cl_2$ requires N, 13·2 per cent.).

8-*β-Aminoethylaminoquinoline*,



$NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$.

It is prepared from 8-aminoquinoline and β-bromoethylphthalimide. It melts at 241°. (Found: N, 16·4. $C_{11}H_{15}N_3Cl_2$ requires N, 16·3 per cent.).

8-*γ-Aminopropylaminoquinoline*.—It is obtained as above from 8-aminoquinoline and γ-bromopropylphthalimide. It melts at 247°. (Found: N, 15·5. $C_{12}H_{17}N_3Cl_2$ requires N, 15·3 per cent.).

THE BRAHMACHARI RESEARCH INSTITUTE,
82-3, CORNWALLIS STREET, CALCUTTA.

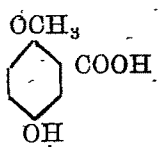
Received August 17, 1931.

A Synthesis of 5-hydroxy-2-methoxybenzoic Acid.

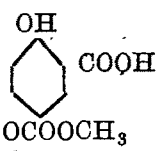
By Andrew Norman Meldrum and Madhavlal Sukhlal Shah.

Sulphosalicylic acid which the authors have shown to be 5-sulpho-2-hydroxybenzoic (*J. Chem. Soc.*, 1923, **123**, 1986 ; *cf.* Stewart, *J. Chem. Soc.*, 1922, **121**, 2555) might be expected, on fusion with potassium hydroxide, to give 2:5-dihydroxybenzoic acid (I). Remsen, however, found that sulphosalicylic acid on fusion with potash gave salicylic acid and phenol (*Annalen*, 1875, **179**, 107). In repeated experiments with the methyl ether of sulphosalicylic acid the authors had a similar experience: fusion with potassium hydroxide, sodium hydroxide, sodium methylate and sodium acetate gave salicylic acid as the principal product in each case.

The synthesis of 5-hydroxy-2-methoxybenzoic acid was undertaken with a view to recognising it in case it should be formed in the fusion experiments. The difficulty in preparing it was noted by Tiemann and Maxmüller (*Ber.*, 1881, **14**, 1985). It cannot be obtained by the direct methylation of gentisic acid, 2:5-dihydroxybenzoic acid, because the tendency is to produce the 5-methoxy-and 2:5-dimethoxybenzoic acids.



(I)



(II)

Emil Fischer, starting with gentisic acid, by using methylchloroformate, obtained 5-carbomethoxy-2-hydroxybenzoic acid (II) (*Ber.*, 1909, **42** 215). Emil Fischer and Pfeiffer treated this substance with diazo-methane obtaining methyl-5-carbomethoxy-2-methoxybenzoate which on hydrolysis, gave 5-hydroxy-2-methoxybenzoic acid: the acid melted at 155°-56° and gave a greyish violet coloration with ferric chloride solution (*Annalen*, 1912, **389**, 198). The authors have obtained the acid from the 5-amino-compound and find

that it melts at 172° and gives with ferric chlorlde solution a violet coloration that intensifies on standing.

When the methyl ether of salicylic acid was nitrated, two isomeric nitro-acids were produced which were separated by means of their barium and calcium salts ; the procedure was similar to that adopted by Simonsen and Rau (*J. Chem. Soc.*, 1917, **111**, 220). Froelicher and Cohen (*J. Chem. Soc.*, 1922, **121**, 1652) describe three isomeric acids as the products of nitration in presence of acetic anhydride. The authors* find that nitration at different temperatures produces only the 5-and 3-nitro-2-methoxybenzoic acids and that a low temperature, leads to a high percentage of 5-nitro-acid.

5-Nitro-2-methoxybenzoic acid was reduced by ammoniacal ferrous hydroxide (Simonsen and Rau, *loc. cit.*). Froelicher and Cohen (*loc. cit.*) regard ferrous hydroxide as unsatisfactory and recommend the use of stannous chloride: the authors find that ammoniacal ferrous hydroxide reduces the acid smoothly and gives an 89 per cent. yield of the amino-sulphate.

Numerous attempts were made to diazotise the amino-sulphate and then to obtain a phenol without isolation of the diazo-compound but those were unsuccessful. It was thought advisable to isolate the diazo-componnd and then to work carefully with it.

The diazo-sulphate, on separation, was found to possess properties that accounted for the difficulties already encountered in converting it into a phenol. It is unusually stable at 150°; it swells and decomposes. It can be preserved in a blue coloured bottle or a black envelope without decomposition. The solution in water when boiled in absence of light did not decompose and on exposure to light produced a red coloured tar. Finally the substance was converted into a phenol by heating it using fused magnesium chloride as a medium.

The 5-hydroxy-2-methoxybenzoic acid thus obtained melts at 172°, the isomer, 5-methoxy-2-hydroxybenzoic acid, melts at 142°. It was converted into 2:5-dimethoxybenzoic acid melting at 80°. Tiemann and Maxmüller (*loc. cit.*) gave 76°. Emil Fischer and Pfeiffer did not carry out the methylation of their acid melting at 155-56°.

* Dr. J. N. Ray informs us that in 1925 he repeated this work of Froelicher and Cohen at Manchester and arrived at the same conclusion that only two nitro-derivatives were formed. But this result has not been published by him.

EXPERIMENTAL.

Nitration of 2-Methoxybenzoic Acid.—To a solution of 2-methoxybenzoic acid (10 g.) in nitric acid (d 1·4, 25 g.) at 30°, sulphuric acid (30 g.) was added drop by drop ; the solution became orange coloured and some nitrogen peroxide was evolved. After 15 minutes the solution was treated with ice-water (300 c.c.) when a crystalline mass separated which was collected, washed and dried, yield, 13·5 g. It consists of two isomeric nitro-acids.

The two isomeric acids are not very different in solubility ; the barium and calcium salts of the 5-nitro-acid are much less soluble than those of the 3-nitro-acid ; the barium salt is less soluble than the calcium salt. The mixture of acids was repeatedly extracted with boiling water ; finally an acid was left undissolved which crystallised from dilute acetic acid in rectangular plates, m.p. 162-63°, yield, 5 g. This is 5-nitro-2-methoxybenzoic acid. The aqueous solution of the two acids was digested with barium carbonate. The solution gave glossy straw coloured needles in clusters of barium 5-nitro-2-methoxybenzoate. When the latter salt no longer separated, the mother-liquor was acidified and the precipitated acids were collected. On digestion of these acids with water and calcium carbonate, a solution of the calcium salts was obtained from which calcium 5-nitro-2 methoxybenzoate separated in prismatic needles.

The barium and calcium salts together were dissolved in water and the solution was acidified. The 5-nitro acid that separated, was crystallised from water, m.p. 162-63°, yield, 5·3 g. (Found: Equi. wt., 196·9. $C_8H_7O_5N$ requires equi. wt., 197·0).

The mother-liquor, when it ceased to give the calcium salt, was acidified. The 3-nitro-acid that separated was crystallised from water in silky needles, m.p. 196°, yield, 3 g. (Found: Equi. wt., 197·2. $C_8H_7O_5N$ requires equi. wt., 197·0).

It was observed that the proportion of 3-nitro acid increases if nitration is carried out at a higher temperature.

Temp.	5-Nitro-acid.	3-Nitro-acid.
0° (Simonsen and Rau)	83 p.c.	14 p. c.
30-35°	76	22
75-100°	73	25

5-Amino-sulphate-2-methoxybenzoic Acid.—5-Nitro-2-methoxybenzoic acid was reduced by ammoniacal ferrous hydroxide. As this process was found unsatisfactory by Froelicher and Cohen (*loc. cit.*) it is given in detail.

5-Nitro-2-methoxybenzoic acid (40 g.) dissolved in ammonia solution, was treated with a solution of ferrous sulphate (320 g.) in water (700 c.c.); ammonia in excess was then added and the mixture vigorously shaken when it changed colour and finally became yellowish green. The mixture was then heated on a water-bath for two hours and allowed to stand overnight. The ferric hydroxide was removed by filtration and washed with boiling water. The pink coloured filtrate was concentrated, treated with animal charcoal and filtered; the filtrate on acidification with sulphuric acid deposited glistening square plates which did not melt but decomposed at 242°, yield, 38·5 g. With ferric chloride solution the pure amino-sulphate developed a violet coloration which intensified on standing. (Found: N, 6·41; S, 7·25. $(C_8H_9O_3N)_2\ H_2SO_4$ requires N, 6·48; S, 7·4 per cent.).

5-Diazo-sulphate-2-methoxybenzoic Acid.—The finely powdered amino-sulphate (20 g.) was suspended in 10 per cent. sulphuric acid (80 c. c.) cooled and treated with a stream of nitrous acid gas under constant shaking, the mixture being kept below 10°. The amino-sulphate passed into solution and the process was stopped when a trace of it was left undissolved. Air was then bubbled through the solution to remove undissolved nitrous gases. After filtration the solution was poured into absolute alcohol (250 c. c.) and the whole immersed in a freezing mixture. 5-Diazo-sulphate-2-methoxybenzoic acid separated in rectangular plates which were collected, washed with cold absolute alcohol and dried, yield, 18·5 g.

The diazo-sulphate decomposes with evolution of nitrogen and carbon dioxide at 150°. On exposure to light it changes at the surface to a red substance. When kept in a black envelope or a blue coloured bottle it is perfectly stable. (Found: N, 12·5; S, 7·06. $(C_8H_7O_3N_2)_2\ SO_4$ requires N, 12·84; S, 7·05 per cent.).

5-Hydroxy-2-methoxybenzoic Acid.—After several experiments the following process was adopted. $MgCl_2$, $6\ H_2O$ (200 g.) was placed in a casserole and heated to 145°; a solution of 5-diazo-sulphate-2-methoxybenzoic acid (8 g.) in water (15 c. c.) was then added drop by drop, keeping the mixture well-stirred. Nitrogen escaped freely and within a short time a pinkish white mass collect-

ed on the surface. (Tarry products begin to separate if the mixture is not well-stirred and if the solution is added quickly). The whole mass was then heated for 15 minutes and the temperature allowed to rise to 155°. The mixture after cooling was dissolved in hot water and the solution was neutralised with ammonia, decolorised with animal charcoal and filtered. The filtrate on acidification gave needle-shaped crystals, yield, 1·8 g. For analysis the substance was recrystallised from hot water when it separated in glistening needles, m.p. 172°. The acid gave, with ferric chloride solution, a violet coloration that intensified on standing. It is easily soluble in methyl alcohol, ethyl alcohol and acetone and moderately soluble in benzene and toluene. (Found: C, 57·25; H, 4·65; equi. wt, 169, 168. $C_8H_8O_4$ requires C, 57·1; H, 4·78 per cent; equi. wt., 168).

The *barium* salt is produced on digestion with water and barium carbonate, crystallises in tufts of needles containing 3 molecules of water. (Found: Ba, 25·96; H_2O, 10·52. $(C_8H_7O_4)_2$ Ba, 3 H_2O requires Ba, 26·15; H_2O, 16·3 per cent.). The barium salt on treatment with the equivalent amount of sulphuric acid liberated the original acid which melted, when heated alone or mixed with the above specimen, at 172° and gave with ferric chloride solution a violet coloration that intensified on standing.

2:5-*Dimethoxybenzoic Acid.*—5-Hydroxy-2-methoxybenzoic acid (0·5 g.) was dissolved in dilute sodium hydroxide solution and treated alternately with dimethylsulphate (8 c.c.) and 20 p. c. sodium hydroxide solution (25 c. c.). More sodium hydroxide (10 c c.) was then added and the ester hydrolysed by heating on a water-bath. On cooling, sodium-25-dimethoxybenzoate separated in fibrous condition; it was collected, dissolved in hot water and acidified with hydrochloric acid. 2:5-Dimethoxybenzoic acid separated in shining needles, m.p. 80°, yield, 0·45 g. It was crystallised from water for analysis. (Found: Equi. wt., 182·9. $C_9H_{10}O_4$ requires equi. wt., 182).

Summary.

1. The synthesis of 5-hydroxy-2-methoxybenzoic acid has been accomplished from the corresponding amino-compound.

2. 5-Hydroxy-2-methoxybenzoic acid and 5-amino-sulphate-2-methoxybenzoic acid are found to give with ferric chloride solution a violet coloration which intensifies on standing.

8. A new method for converting an unusually stable diazo-compound into a phenol, namely treatment with fused magnesium chloride, is described.

Further work is in progress with a view (*a*) to account for the violet coloration which 5 amino and 5-hydroxy-2-methoxybenzoic acids produce with ferric chloride, and (*b*) to generalise the use of fused magnesium chloride in the conversion of stable diazo-compounds into phenols.

THE MADHAVLAL RANCHHODLAL SCIENCE INSTITUTE,
GUJARAT COLLEGE, AHMEDABAD.

Received July 24, 1931

Studies in the Optical Properties of Chlorophyll. Part I. Absorption of Light by Solutions and Suspensions of Chlorophyll-α and Chlorophyll-β and their Mixtures.

By J. C. Ghosh and Sunil Behari Sen-Gupta.

The absorption spectra of solutions of chlorophyll have been examined qualitatively by a large number of investigators. The spectragrams obtained by Wilstätter and Stoll show that solutions of chlorophyll-α have seven sharply defined absorption bands in the visible, of which the three strong bands are in the red, indigo blue and violet with band heads at about 660$\mu\mu$, 460$\mu\mu$, and 430$\mu\mu$. The absorption spectra of chlorophyll-β solutions show nine bands in the visible, of which the strongest have band heads at about 640$\mu\mu$, 455$\mu\mu$ and 430$\mu\mu$.

Tsvett (*Ber. Deut. bot. Ges.*, 1907, **25**, 388; *ibid.*, 1918, **36**, 74; *Z. wiss. Mikrosk.*, 1888, **5**, 289), and Warburg and Nigelein (*Z. Phys. Chem.*, 1923, **106**, 195), determined the extinction coefficients of chlorophyll solutions quantitatively by spectrophotometric methods, but evidently they did not use absolutely pure samples of chlorophyll. Thus Warburg and Nigelein extracted the pigments from the *algae chlorella*, and determined the extinction coefficient for a solution of 0·2 g. of dry pigment, which contained both chlorophyll-α and-β in 1000 c.c. of solution by the König-Marten spectrophotometer.

In this paper, measurements of extinction coefficients of pure samples of chlorophyll-α and chlorophyll-β and also their mixtures in states of solution and suspension will be described. The results obtained enable us to calculate the total chlorophyll content in a sample of a liquid and also the ratio of chlorophyll-α to-β.

Experimental.

Pure samples of chlorophyll-α and chlorophyll-β were very kindly prepared for the purpose of this investigation by Prof. Stoll. Both chlorophyll-α and-β dissolve in acetone to form molecularly disperse

solutions. Suspensions of chlorophyll in water containing 1% acetone were prepared by dissolving the required quantity of chlorophyll in one c. c. of acetone and adding 99 c. c. of water.

Emulsions of chlorophyll in water were prepared with the help of lecithin as follows:—Chlorophyll was dissolved in absolute alcohol, while lecithin was dissolved in alcohol-ether mixtures in the ratio of 5:1. The two solutions were mixed together and the requisite quantity of pure water was added. The suspension was dialysed for 8 weeks in a stream of pure water, with the addition of chloroform to prevent the growth of the fungus. The dialysed supension did not contain alcohol or ether. Many plant physiologists are of opinion that the chlorophyll in plant leaves exists in a state of true solution in lipoid bodies, which in their turn remain suspended in aqueous medium as fine colloidal particles. Suspension of chlorophyll in water containing lecithin may in a sense be considered to have similar optical properties to those of chloroplasts in the plant leaves.

For the determination of the extinction coefficients, a König-Marten spectrophotometer was used. The wave-length scale of the apparatus was calibrated by the lines from a mercury lamp. A rectangular double absorption glass cell, with chlorophyll solution in in one chamber and pure water in the other, was placed on the spectrometer table and the molar extinction coefficient was calculated from the equation

$$\epsilon = \frac{\log \tan A - \log \tan A'}{c.d},$$

where, c denotes the molar concentration of chlorophyll in solution and suspension and d, the thickness of the cell, expressed in millimeters and A and A' are respectively the final and initial angles.

The thickness of the solution was 1 cm. and the strength of chlorophyll solution or emulsion never exceeded $M/20{,}000$. The concentration of lecithin used did not exceed $M/20{,}000$. Lecithin was purified according to the directions of Levene and Rolf (*J. Biol. Chem.*, 1927, **72**, 587).

The experimental data are recorded in Tables I, II, III and are represented graphically in Figs. 1, 2, 3, respectively. The molecular extinction coefficients given below are to be multiplied by 10^4 and are given in the following tables against the corresponding wave-lengths.

TABLE I.

Chlorophyll-α and-β and their mixtures in acetone solutions.

	1	2	3	4	5	6	7	8	9	10	11
Wave length.	100 p.c. (α)	90 p.c. 10 p.c.	80 p.c. 20 p.c.	70 p.c. 30 p.c.	60 p.c. 40 p.c.	50 p.c. 50 p.c.	40 p.c. 60 p.c.	30 p.c. 70 p.c.	20 p.c. 80 p.c.	10 p.c. 90 p.c.	100 p.c. (β)
6900	·0153	·0153	·0153	·0153	·0153	·0142	·0142	·0142	·0142	·0142	·0106
6800	·0395	·0374	·0350	·0332	·0332	·0311	·0258	·0258	·0226	·0205	·0184
6700	·0850	·0800	·0760	·0760	·0635	·0592	·0544	·0502	·0452	·0412	·0350
6600	·1423	·1355	·1277	·1186	·1107	·1022	·0944	·0866	·0800	·0718	·0635
6500	·0920	·0920	·0920	·0920	·0920	·0920	·0920	·0920	·0920	·0920	·0940
6400	·0544	·0584	·0615	·0650	·0688	·0702	·0755	·0800	·0828	·0870	·0900
6300	·0452	·0472	·0472	·0500	·0500	·0525	·0525	·0550	·0550	·0550	·0600
6200	·0427	·0427	·0427	·0427	·0427	·0427	·0427	·0427	·0427	·0427	·0430
6100	·0412	·0412	·0412	·0412	·0412	·0412	·0412	·0412	·0412	·0412	·0412
6000	·0345	·0345	·0345	·0345	·0374	·0374	·0374	·0374	·0374	·0395	·0395
4800	·0147	·0230	·0300	·0387	·0464	·0611	·0624	·0700	·0787	·0861	·0940
4700	·0147	·0390	·0600	·0820	·1034	·1245	·1451	·1675	·1895	·2165	·2316
4600	·0345	·0619	·0900	·1168	·1400	·1884	·2000	·2264	·2540	·2810	·3067
4400	·1820	·1472	·1624	·1775	·1925	·2125	·2240	·2382	·2540	·2700	·2838
4350	·2199	·2250	·2321	·2321	·2400	·2420	·2440	·2500	·2600	·2722	·2756

TABLE II.

Aqueous suspension of chlorophyll-α and-β and their mixtures in 1 % acetone.

	1	2	3	4	5	6	7	8	9	10	11
Wave-length	100 p.c. (α)	90 p.c. 10 p.c.	80 p.c. 20 p.c.	70 p.c. 30 p.c.	60 p.c. 40 p.c.	50 p.c. 50 p.c.	40 p.c. 60 p.c.	30 p.c. 70 p.c.	20 p.c. 80 p.c.	10 p.c. 90 p.c.	100 p.c. (β)
6900	·0775	·0720	·0643	·0600	·0551	·0500	·0431	·0384	·0352	·0270	·0217
6800	·1050	·0980	·0910	·0840	·0775	·0700	·0628	·0558	·0485	·0420	·0348
6700	·0950	·0911	·0876	·0800	·0785	·0756	·0717	·0690	·0640	·0600	·0560
6600	·0748	·0748	·0735	·0735	·0720	·0720	·0720	·0700	·0700	·6880	·0688
6500	·0588	·0588	·0605	·0605	·0633	·6330	·0683	·0656	·0656	·0683	·0688
6400	·0558	·0558	·0558	·0558	·0558	·0558	·0558	·0558	·0558	·0558	·0580
6300	·0134	·0434	·0434	·0434	·0434	·0434	·0434	·0434	·0434	·0484	·0434
6200	·0412	·0412	·0412	·0412	·0412	·0388	·0388	·0388	·0388	·0388	·0365
6100	·0348	·0348	·0348	·0348	·0348	·0348	·0348	·0348	·0348	·0355	·0355
6000	·0296	·0296	·0296	·0296	·0296	·0296	·0296	·0296	·0296	·0312	·0348
4900	·0515	·0561	·0630	·0700	·0760	·0840	·0880	·0940	·1000	·1050	·1126
4800	·0600	·0700	·0800	·0910	·1060	·1126	·1224	·1335	·1438	·1500	·1640
4600	·0820	·0921	·1027	·1101	·1204	·1320	·1400	·1510	·1600	·1702	·1806
4400	·1500	·1550	·1580	·1620	·1640	·1660	·1660	·1752	·1752	·1824	·1860
4350	·2175	·2175	·2175	·2175	·2175	·2041	·2041	·2041	·2041	·2041	·1986

TABLE III.

Molecular extinction coefficient of chlorophyll-α and-β emulsions and their mixtures in M/32000 lecithin (after dialysis).

Wave-length	1 100 p.c. (α)	2 90 p.c. 10 p.c.	3 80 p.c. 20 p.c.	4 70 p.c. 30 p.c.	5 60 p.c. 40 p.c.	6 50 p.c. 50 p.c.	7 40 p.c. 60 p.c.	8 30 p.c. 70 p.c.	9 20 p.c. 80 p.c.	10 10 p.c. 90 p.c.	11 100 p.c. (β)
6900	·0447	·0424	·0400	·0378	·0353	·0330	·0307	·0307	·0271	·0238	·0218
6800	·0632	·0600	·0567	·0535	·0500	·0480	·044	·0400	·0375	·0343	·0311
6700	·0757	·0717	·0688	·0658	·0620	·0600	·055	·0510	·0480	·0446	·0412
6600	·0652	·0652	·0630	·0630	·0608	·0584	·0584	·0570	·0570	·0544	·0554
6500	·0447	·0447	·0447	·0447	·0447	·0471	·0471	·0500	·0500	·0500	·0540
6400	·0311	·0330	·0360	·0371	·0386	·0433	·0451	·0462	·0480	·0480	·0500
6300	·0280	·0280	·0280	·0280	·0307	·0320	·0320	·0320	·0350	·0350	·0380
6200	·0280	·0280	·0280	·0280	·0290	·0290	·0290	·0290	·0330	·0330	·0330
6100	·0215	·0225	·0225	·0243	·0243	·0256	·0256	·0271	·0271	·0311	·0311
6000	·0170	·0182	·0200	·0200	·0220	·0220	·0256	·0256	·0285	·0285	·0285
4900	·0311	·0360	·0400	·0457	·0500	·0551	·0602	·0653	·0705	·0757	·0800
4800	·0311	·0810	·0452	·0521	·0600	·0665	·0734	·0800	·0875	·0945	·1016
4600	·0361	·0500	·0633	·0770	·0900	·1043	·1177	·1221	·1450	·1600	·1722
4400	·0600	·0712	·0825	·0930	1044	·1162	·1226	·1375	·1500	·1600	·1722
4350	·1068	·1150	·1200	·1250	·1300	·1351	·1450	·1498	·1585	·1700	·1800

Similar experiment was done with the same results in $M/2000$ lecithin.

TABLE IV.

Chlorophyll-a emulsion in lecithin.

Concentration of lecithin.

Wave-length.	*M*/2000	*M*/4000	*M*/8000	*M*/16000	*M*/3200
6900	·0437	·0437	·0457	·0437	·0447
6800	·0620	·0620	·0620	·0620	·0632
6700	·0734	·0734	·0756	·0756	·0756
6600	·0627	·0627	·0627	·0627	·0630
6500	·0447	·0147	·0447	·0447	·0447
6400	·0311	·0311	·0311	·0311	·0311
6300	·0280	·0280	·0280	·0280	·0280
6100	·0215	·0215	·0215	·0215	·0215
6000	·0180	·0180	·0180	·0180	·0180
4900	·0311	·0311	·0311	·0311	·0311
4600	·0361	·0361	·0361	·0361	·0361
4400	·0600	·0600	·0600	·0600	·0600
4350	·1120	·1120	·1068	·1068	·1068

TABLE V.

Chlorophyll-β emulsion in lecithin.

Concentration of lecithin.

Wave-length.	*M*/2000	*M*/4000	*M*/8000	*M*/16000	*M*/82000
6900	·0220	·0215	·0215	·0215	·0218
6800	·0307	·0307	·0307	·0307	·0311
6700	·0412	·0412	·0412	·0412	0412
6600	·0544	·0544	·0544	·0544	0544
6400	·0471	·0471	·0500	·0500	·0500
6300	·0380	·0380	·0380	·0380	·0380
6200	·0330	·0330	·0330	·0330	·0330
6100	·0311	·0311	·0311	·0311	·0311
6000	·0265	·0265	·0265	·0265	·0285
4900	·0800	·0800	·0800	·0800	·0800
4800	·1016	·1016	·1016	·1016	·1016
4700	·1400	·1400	·1400	·1374	·1374
4600	·1722	·1722	·1722	·1722	·1722
4400	·1800	·1800	·1780	·1780	·1780
4350	·1930	·1930	·1850	·1800	·1800

FIG. 1.

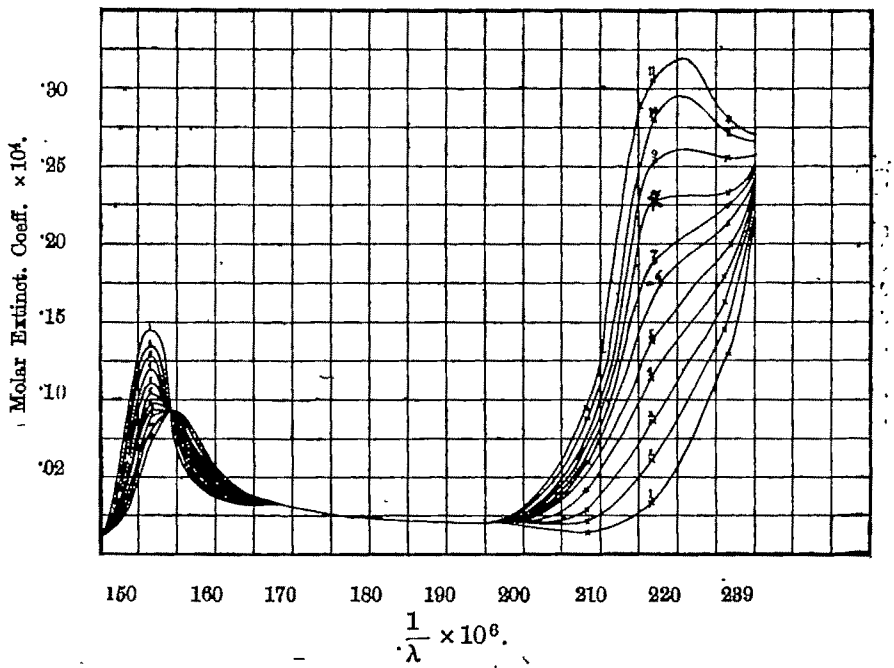

·30
·25
·20
·15
·10
·02
Molar Extinct. Coeff. ×10⁴.
150
160
170
180
190
200
210
220
239
1/λ ×10⁶.

FIG. 2.

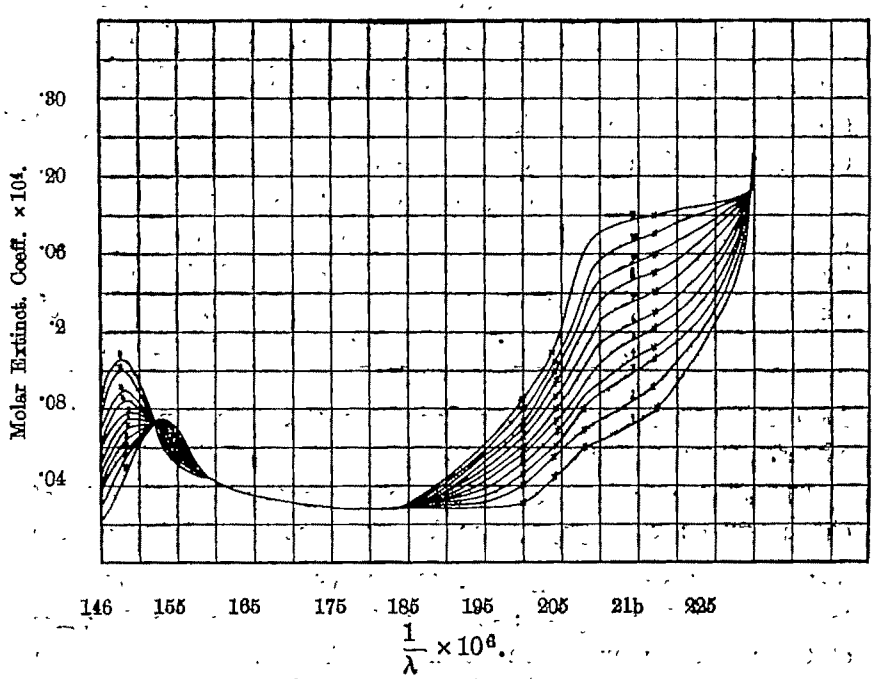
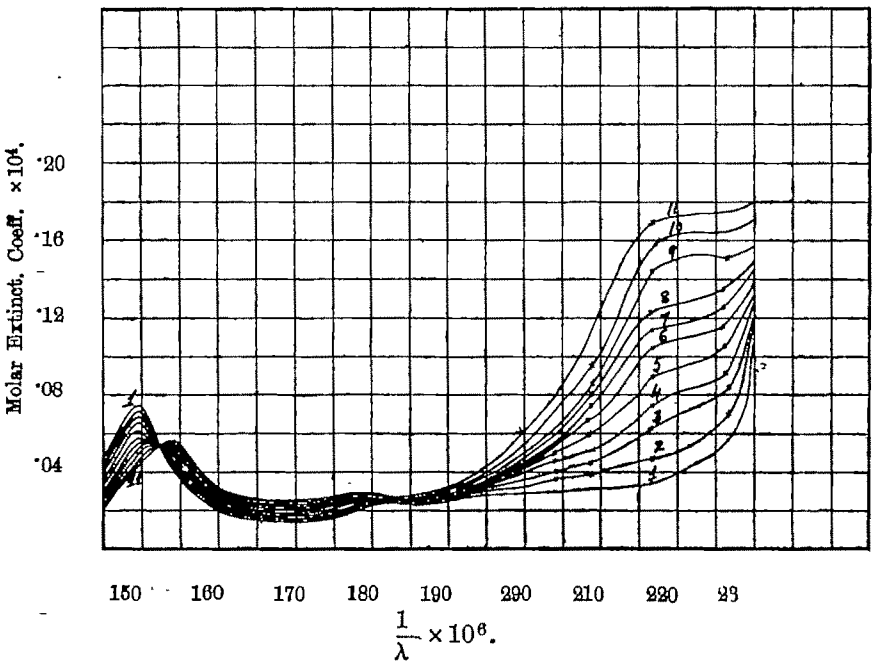

·30
·20
·06
·2
·08
·04
Molar Extinct. Coeff. ×10⁴.
146
155
165
175
185
195
205
215
225
1/λ ×10⁶.

FIG. 8.



It will be seen that, as a general rule, in all solutions of suspensions, chlorophyll-α has a larger extinction coefficient than that of chlorophyll-β for wave-lengths larger than 6400 Å—6300 Å, whereas for smaller wave-lengths, the extinction coefficients of chlorophyll-β become larger than that of chlorophyll-α.

In Fig. 1, the molecular extinction coefficients of acetone solutions of chlorophyll-α and-β, and their mixtures are represented. The molar concentration of any chlorophyll-$(\alpha+\beta)$ solution in acetone can at once be found by observing the extinction coefficient ϵ', which is expressed by $\epsilon'=\frac{\log\tan A-\log\tan A'}{d}$ at $\lambda=6500$Å, where curves from 1 to 11 meet, and dividing the molar extinction coefficient ϵ by ϵ'.

The total chlorophyll concentration being known, the ratio of chlorophyll-α : chlorophyll-β can be ascertained by finding out the molar extinction coefficient at $\lambda=4600$ Å, where for small changes in the ratio of chlorophyll-α : -β, there is a large change in the value of the molecular extinction coefficient. Thus a molar extinction coefficient of chlorophyll-$(\alpha+\beta)$ represented by the point X (8) in

Fig. 1 can be shown by graphical interpolation to have the $\alpha : \beta$ ratio $= 3:7$.

What is true of acetone solutions of chlorophyll is also true of chlorophyll suspensions. Only the wave-lengths where chlorophyll-α and chlorophyll-β have identical values of molecular extinction coefficients are shifted more towards the red. For these suspensions also, the molecular concentration of chlorophyll-$(\alpha+\beta)$ and also of the ratio of α/β can be calculated from extinction coefficient data in precisely the same way as in acetone solutions.

CHEMICAL LABORATORY,
THE UNIVERSITY OF DACCA.

Received August 8, 1931.

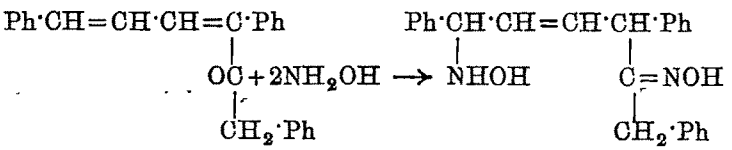
Condensation of Dibenzylketone with Aromatic Aldehydes and Ketones

By Rajendra Nath Sen and Jatindra Lal Nandi.

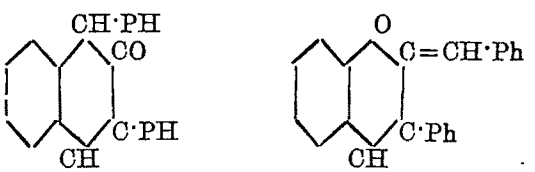
Goldschmiedt and Knöpfer (*Monatsh.*, 1898, **19**, 406), Hertzka *Monatsh.*, 1905, **26**, 227) and Schimetschek (*Monatsh.*, 1906, **27**, 1) studied the condensations of dibenzylketone with different aromatic aldehydes in presence of dry hydrochloric acid gas in ice-cold benzene solution and got in each case the hydrogen chloride additive product of the benzylidenedibenzylketone, which on heating, decomposed in most cases and only in a few cases gave off hydrochloric acid yielding the unsaturated product. Goldschmiedt and Spitzauer (*Monatsh.*, 1903, **24**, 270) isolated benzylidenedibenzylketone by the action of strong alcoholic solution of caustic potash on the hydrochloride. Goldschmiedt and Knöpfer (*Monatsh.*, 1899, **20**, 734) using dilute potassium hydroxide obtained an addition product of two molecules of benzaldehyde with one molecule of dibenzylketone. In the present investigation the condensation of dibenzylketone with aromatic aldehydes and ketones have been further investigated by using at ordinary temperature (*i*) 60 p.c. alcoholic caustic potash solution and (*ii*) dry hydrochloric acid gas and very satisfactory results have been obtained.

Benzaldehyde, *o*-nitrobenzaldehyde and cinnamic aldehyde in methyl alcoholic solution condense readily at ordinary temperature with dibenzylketone in presence of 60 p.c. alcoholic potassium hydroxide; one molecule of the ketone condensing with one molecule of the aldehyde, forming the benzylidene derivatives in good yields. It is interesting to note that dibenzylketone reacts with two molecules of *o*-nitrobenzaldehyde under conditions in which it reacts with only one molecule of benzaldehyde or cinnamic aldehyde.

Cinnamylidenedibenzylketone, m.p. 110°, reacts in an interesting manner with two molecules of hydroxylamine, which can be satisfactorily explained by Thiele's theory of conjugated double bonds—

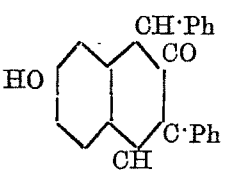


The hydroxyaldehydes, *e.g.*, salicyladehyde, resorcylaldehyde and *o*-hydroxybenzaldehyde, which appear not to react readily in presence of 60 p.c. alcoholic potash solution, have been successfully condensed with dibenzylketone in presence of dry hydrochloric acid gas at the ordinary temperature. The salicylaldehyde compound is completely insoluble in caustic alkali, even on boiling, which shows that the hydroxyl group takes part in the reaction, yielding product (I) or (II)



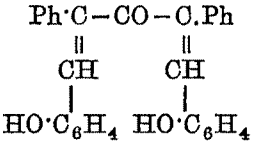
(I) (II)

But as the condensation product gives a hydrazone (m.p. 50°) the formula (I) is the most probable one; it is however remarkable that it behaves in the ketonic and not in the enolic form. The resorcylaldehyde compound yields a monobenzoyl derivative (m.p. 110°), and a hydrazone (m.p. 104°); hence it may be given the following structure:



The condensation product of *p*-hydroxybenzaldehyde with dibenzylketone is deep violet, readily soluble in caustic alkali and giving a

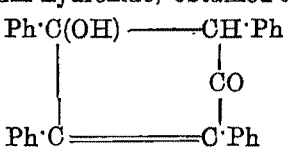
dibenzoyl derivative (m.p. 158°), a hydrazone (m.p. 120°) and an oxime (m.p. 131-33°): it may therefore be represented thus:



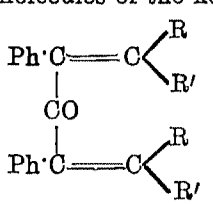
It may be observed in this connection that chloro-*p*-hydroxybenzyldibenzylketone was obtained by Schimetschek (*loc. cit.*) by the action of hydrochloric acid on a mixture of dibenzylketone and *p*-hydroxybenzaldehyde dissolved in acetic acid; only one molecule of the aldehyde condensed with one molecule of dibenzylketone.

m-Hydroxybenzaldehyde under similar conditions condensed with dibenzylketone yielding two products insoluble in caustic alkali; one, soluble in ether melting at 114-16° and the other sparingly soluble in ether and does not melt up to 240°. These have not been further investigated.

The condensation of dibenzylketone with ketones appears not to have been studied much before. Henderson and Corstorphine (*J. Chem. Soc.*, 1901, **79**, 1256) by heating a mixture of dibenzylketone and benzil for a short time on the water-bath with 33 p.c. aqueous potassium hydroxide, obtained tetraphenyl*cyclo*pentenolone.

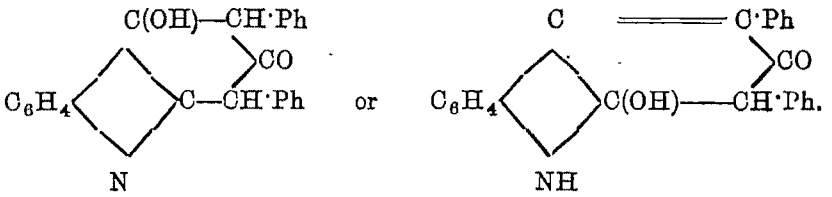


Dibenzylketone has now been condensed with typical ketones such as acetone, acetophenone, benzophenone, by using 60 p.c. alcholic caustic potash solution, one molecule of dibenzylketone readily condensing with two molecules of the ketone with a good yield.



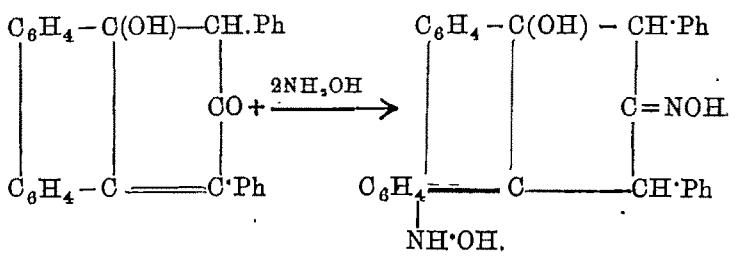
The diketones, isatin and phenathraquinone, have also been condensed with dibenzylketone by the action of 60 p. c. alcoholic caustic potash solution, and compounds, similar to the condensation product of benzil with dibenzylketone of Henderson and Corstorphine (*loc. cit.*), have been obtained.

The light yellow condensation product of isatin and dibenzylketone melts at 255°-57°, and is soluble in caustic alkali. The compound gives a dibromide, which does not melt up to 270°. The structure of the compound is



It gives a perfectly white oxime, which does not melt even when heated up to 280°

The phenanthraquinone condensation product is soluble in caustic alkali on heating and like cinnamylidenedibenzylketone reacts with two molecules of hydroxylamine.



Experimental.

Benzylidenedibenzylketone.—Dibenzylketone (2·1 g.) and benzaldehyde (1·06 g.) are dissolved in methyl alcohol (15 c.c.) and a few drops of 60 p.c. alcoholic potassium hydroxide solution are added. After three hours the mixture is poured into water and the precipitate thoroughly washed with hot water and crystallised from dilute alcohol as colourless microcrystalline powder, m.p. 86°. It is identical with the compound isolated by Goldschmiedt and Spitzauer (*loc. cit.*), yield 75 p.c. It is soluble in alcohol, acetone, ether, benzene, chloroform, carbon tetrachloride and nitrobenzene. (Found: C, 88·52; 88·5; H, 5·99. $C_{22}H_{18}O$ requires C, 88·59; H, 6·04 per cent.).

The phenylhydrazone crystallises from dilute alcohol as a microcrystalline powder, m.p. 90-91°. (Found: N, 7·19, 7·08. $C_{28}H_{24}N_2$ requires N, 7·21 per cent.).

Cinnamylidenedibenzylketone is prepared from dibenzylketone (3·15 g.), cinnamic aldehyde (dissolved in methyl alcohol 15 c.c.) with a few drops of 60 p.c. alcoholic caustic potash solution. After two hours the mixture is poured into water and the yellow precipitate washed with water and crystallised from dilute alcohol as a microcrystalline powder melting at 110°, yield 79 p.c. It is soluble in alcohol, acetone, chloroform, carbon tetrachloride, benzene, ether, nitrobenzene and glacial acetic acid. (Found: C, 88·76, 88·72; H, 6·15, 6·09. $C_{24}H_{20}O$ requires C, 88·38; H, 6·17 per cent.).

The hydrazone, prepared as usual, crystallises from dilute alcohol as a chocolate-coloured microcrystalline powder melting at 120°. (Found: N, 6·78. $C_{30}H_{26}N_2$ requires N, 6·76 per cent.).

The oxime, obtained as a yellow powder, melts at 150-51°. (Found: N, 7·48, 7·41. $C_{24}H_{24}O_2N_2$ requires N, 7·52 per cent.).

Di-ortho-*nitrobenzylidenedibenzylketone* is prepared by the condensation of 2 molecules of *o*-nitrobenzaldehyde and one molecule of dibenzylketone with a few drops of 60 p.c. alcoholic caustic potash solution. It is crystallised from alcohol as small orange-red needles, which become brick-red at 215° and melt at 226°. It is soluble in acetone, alcohol, benzene, ether, chloroform and carbon tetrachloride. (Found: N, 5·80, 5·75. $C_{29}H_{20}N_2O_5$ requires N, 5·88 per cent.).

The phenylhydrazone, prepared in the usual manner, is obtained as a microcrystalline powder melting at 100°. (Found: N, 9·74, 9·68. $C_{35}H_{26}O_4N_4$ requires N, 9·89 per cent.).

Condensation product of Salicylaldehyde and Dibenzylketone.—Dry hydrochloric acid gas is passed for an hour and a half at ordinary temperature into a solution of dibenzylketone (3·15 g.) and salicylaldehyde (1·88 g.) in methyl alcohol (20 c.c.), when a yellow solid separates out. The mixture is then poured into water and the solid is powdered and washed with dilute caustic soda solution. It is obtained as a microcrystalline powder melting at 106° from dilute alcohol. It is soluble in alcohol, acetone, benzene, nitrobenzene, ether and chloroform. (Found: C, 88·89, 89·09; H, 5·89, 5·89. $C_{22}H_{16}O$ requires C, 89·18; H, 5·40 per cent.).

The phenylhydrazone is obtained as fine powder melting at 50° from dilute alcohol. (Found: N, 7·12, 7·17. $C_{28}H_{22}N_2$ requires N, 7·25 per cent.).

Condensation product of Resorcylaldehyde and Dibenzylketone.—It is obtained as in the case of salicylaldehyde. The brown mass is dissolved in caustic alkali solution, precipitated with acid, an

obtained as brick-red powder melting at 151-52° from dilute alcohol. It is soluble in alcohol, acetone, chloroform, benzene, nitrobenzene, ether. and caustic alkali. (Found: C, 84·45, 84·47; H, 5·08, 5·08. $C_{22}H_{16}O_2$ requires C, 84·61; H, 5·12 per cent.).

The *phenylhydrazone*, is obtained as a red microcrystalline powder melting at 104-05° from dilute alcohol. (Found: N, 6·79. $C_{28}H_{22}ON_2$ requires N, 6·96 per cent.).

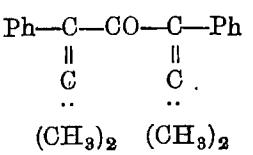
The *benzoyl* derivative, prepared by Schotten-Baumann process, is obtained as a microcrystalline powder melting at 110-11° from alcohol. (Found: C, 83·48, 83·47; H, 4·79. $C_{29}H_{20}O_3$ requires C, 83·65; H, 4·8 per cent.).

Di-p-hydroxydibenzylidinedibenzylketone is prepared by passing dry hydrochloric acid gas at ordinary temperature to a mixture of dibenzylketone (2·1 g.), *para*-hydroxybenzaldehyde (2·5 g.), dissolved in methyl alcohol (15 c.c.) when a deep violet semi-solid mass is obtained. The whole mass solidifies on the addition of a little water. It is powdered, washed with carbon tetrachloride and hot water and obtained from dilute alcohol as deep violet microcrystalline powder melting at 170°. (Found: C, 83·16; H, 5·19. $C_{29}H_{22}O_3$ requires C, 83·25; H, 5·26 per cent.).

The phenyl hydrazone is obtained as a microcrystalline yellow powder melting at 120-22° from dilute alcohol. (Found: N, 4·99. $C_{35}H_{28}O_2N_2$ requires N, 5·51 per cent.).

The oxime crystallises from dilute alcohol and is obtained as a microcrystalline powder melting at 181°. (Found: N, 3·08. $C_{29}H_{27}O_3N$ requires N, 3·23 per cent.).

The *dibenzoyl* derivative, crystallises from dilute acetone and is obtained as a microcrystalline powder melting at 158°. (Found: C, 82·29; H, 4·79. $C_{43}H_{30}O_5$ requires C, 82·42; H, 4·79 per cent.).



Bis-isopropylidenedibenzylketone.—A few drops of 60 p. c. alcoholic caustic potash solution are added to a mixture of dibenzylketone (3·15 g.) and acetone (1·87 g.) dissolved in alcohol (14 c.c.). After fours hours the solution is poured into acidified water and the yellow precipitate washed with water and crystallised from dilute alcohol as

a powder melting at 91-92°. (Found: C, 86·78; H, 7·49. $C_{21}H_{22}O$ requires C, 86·89; H, 7·58 per cent.).

The phenylhydrazone is obtained as a chocolate coloured microcrystalline powder melting at 99° from dilute alcohol. (Found: N, 7·18. $C_{27}H_{28}N_2$ requires N, 7·36 per cent.).

The *oxime* crystallises from dilute alcohol as a light brown microcrystalline powder melting at 102°. (Found: N, 4·51. $C_{21}H_{23}ON$ requires N, 4·58 per cent.).

Bis-phenylethylidenedibenzylketone is prepared from dibenzylketone and acetophenone in the same manner as with acetone. The pasty mass, obtained on pouring the mixture into water, is extracted with carbon tetrachloride and the semi-solid left on removing the solvent is alternately dissolved in alcohol and acetone and poured into water, when a yellow precipitate is obtained. It is finally obtained as a microcrystalline powder from dilute alcohol melting at 95°. (Found: C, 89·71; H, 6·08. $C_{31}H_{26}O$ requires C, 89·85; H, 6·18 per cent.).

The phenyl hydrazone is obtained as a brown powder melting at 106-07° from dilute alcohol. (Found: N, 5·50. $C_{37}H_{32}N_2$ requires N, 5·55 per cent.).

Bis-phenylbenzylidenedibenzylketone is prepared from dibenzylketone and benzophenone. The method of preparation and purification is the same as in the case of acetophenone; yellow microcrystalline powder, m.p. 91-92°. (Found: C, 91·38; H, 5·49. $C_{41}H_{36}O$ requires C, 91·44 ; H, 5·49 per cent.).

Condensation product of Isatin and Dibenzylketone.—To a solution of dibenzylketone (4 2 g.) and isatin (3 g.), in alcohol (40 c. c.), a few drops of 60 p. c. alcoholic caustic potash solution are added and after three hours the solution is poured into water and acidified with dilute hydrochloric acid, when a light yellow precipitate is obtained. It is washed with hot water and obtained as a light yellow microcrystalline powder melting at 255-57°. It is soluble in pyridine, nitrobenzene, glacial acetic acid and caustic alkali and sparingly in alcohol, acetone and chloroform. (Found: N, 3·93. $C_{23}H_{16}O_2N$ requires N, 4·14 per cent.).

The oxime is colourless and does not melt when heated up to 280°. (Found: N, 7·46. $C_{23}H_{18}O_2N_2$ requires N, 7·90 per cent.).

The dibromide, obtained by adding bromine water to the pyridine solution of the compound, is obtained as a grey crystalline powder from dilute acetone. It does not melt when heated up to 270°.

(Found: Br, 31·80, 31·41. $C_{23}H_{17}O_2NBr_2$ requires Br, 32·06 per cent.).

Condensation product of Dibenzylketone with Phenanthraquinone.—Dibenzylketone (5·1 g.), phenanthraquinone (2·08 g.) are dissolved in benzene (50 c. c.) and a few drops of 60 p. c. alcoholic caustic potash are added. After five hours, the benzene is driven off, the solid is dissolved in alcohol and the solution poured in acidified water, when a yellow compound is obtained. It is finally crystallised from dilute alcohol and obtained as a yellow microcrystalline powder, which turns brown at 84° and melts at 102-103°. It is soluble in alcohol, acetone, benzene, chloroform carbontetrachloride, ether and sparingly soluble in caustic alkali on boiling. (Found: C, 86·60, H, 4·88. $C_{29}H_{20}O_2$ requires C, 87·00; H, 5·00 per cent.).

The oxime is obtained as a microcrystalline powder melting at 98° from dilute alcohol. (Found: N, 6·06. $C_{29}H_{24}O_3N_2$ requires N, 6·25 per cent.).

The hydrazone crystallises from dilute alcohol and is obtained as a crystalline powder melting at 80°. (Found: N, 5·51. $C_{35}H_{28}ON_2$ requires N, 5·71 per cent.).

The dibromide, obtained by adding bromine to the compound, dissolved in chloroform, crystallises from dilute acetone as small orange-red prisms melting at 148-50°. (Found: Br, 38·36. $C_{29}H_{20}O_2Br_2$ requires Br, 28·57 per cent.).

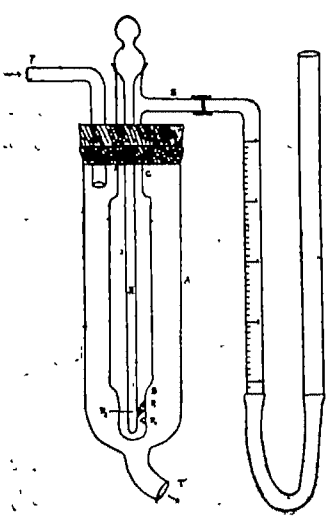
CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Received July 2, 1931.

A Semi-Micro Modification of Victor Meyer's Method for the Determination of Vapour Densities.

By S. Lakshminarayan and U. Mudalagiri Nayak.

Few attempts appear to have been made to modify Victor Meyer's method so as to make it suitable for the determination of the vapour densities of very small quantities of substances. The elegant modifications due to Nernst (*Z. Elektrochem.*, 1903, **9**, 622), Löwenstein (*Z. Phys. Chem.*, 1906, **54**, 707) and Wartenberg (*Ber.*, 1906, **39**, 381; *Z. anorg. Chem.*, 1908, **56**, 320) are useful for the investigation of vapour densities at high temperatures. Recently Niederl (*Z. anal. Chem.*, 1929, **77**, 169) has evolved a micro method, suitable for ordinary ranges of temperature. According to this method, the entire vapourising vessel is filled with mercury and in a preliminary experiment, the amount of mercury expelled from the apparatus, owing to thermal expansion for unit rise of temperature, is ascertained. A sealed capillary containing a weighed amount of the liquid (5mg.) is prepared.



After breaking the tip, it is introduced into the apparatus which is then heated to a known temperature above the boiling point of the liquid under investigation. The expelled mercury is collected and weighed. The difference between this and the amount of mercury expelled owing to thermal expansion corresponds to the vapour liberated. From these data, the molecular weight is calculated. This method lacks, however, the simplicity of Victor Meyer's original macro method, and no other work on these lines appears in the literature.

The modification described here retains the simplicity of the original method while adapting it to measurements on a semi-micro scale.

The apparatus used is shown in the accompanying figure. It consists of a tube A, 9 cm. long and 2 cm. diameter. To its lower end is fused a short tube B, 4 cm. long, 1 cm. diameter, provided with two inward projections P_1 and P_2. To the other end of A is fused a tube C, 6 cm. long and 7 mm. diameter, having a side tube S, fused near its open end.

The breaking rod R, is made out of 4 mm. glass rod, which is thickened near one end and ground to fit into the top portion of C. This rod reaches almost to the bottom of B and is provided with a small blob of glass P_3, so that when the glass rod is fixed in position, P_3 is midway between P_1 and P_2. This corresponds to the breaking device in Newth's ozone apparatus. The fused capillary containing the liquid rests at the bottom of B and is held in position by the three projections P_1, P_2, P_3. By rotating the rod R, the capillary can be easily broken.

The displaced air is collected over mercury in a graduated tube of 5 c. c. capacity. This tube is graduated to 0·1 c. c., the interval between successive graduations corresponding to a length of 5 mm. This can be estimated to a tenth, thus enabling an accuracy of 0·01 c. c. being attained in the estimation of the volume of the air displaced. The ungraduated top portion of the measuring tube is bent at right angles and connected to the side tube S, by means of pressure tubing. A levelling tube is attached to the other end of the measuring tube by a piece of stout rubber tubing.

The apparatus is surrounded by an outer vapour jacket and fixed in position therein by a split cork. Steam is led in through T, and condensed water drips out through T'. The tube T, the side tube S and the ungraduated top portion of the measuring tube are wound round with asbestos string to prevent fluctuations of volume due to a stray gust of hot air from the vicinity of the burner.

A slender capillary of about 2 mm. diameter is prepared and one end is melted down to a rod of about 1 cm. length and 1 mm. diameter which serves as a handle. The other end is drawn out into a fine capillary. In the case of liquids with low molecular weights less than 10 mg. of the liquid was used, the weighing being done correct to 0·01 mg. with a Bunge short beam balance, In other cases correspondingly greater quantities (up to 20 mg.) were used,

the weights being determined correct to 0·1 mg. In any case a sufficient amount of liquid was taken to give a displacement of about 2 to 4 c. c. of air. After filling the capillary with the liquid in the usual manner, the open end was sealed.

The capillaries thus prepared were found to be sufficiently strong and did not burst spontaneously even when heated to a temperature of 40-50 degrees over the boiling point of the liquid.

The prepared capillary was dropped in and fixed in position by proper adjustment of the breaking rod. The apparatus was placed in the steam jacket and heated. An asbestos millboard was placed over the split cork so as to deflect the hot air currents and another was placed between the jacket and the measuring tube.

The levelling tube was adjusted. Generally it was found that thermal equilibrium was established in the course of 5 minutes after the commencement of vigorous boiling of the heating liquid, the mercury level remaining sensibly steady thereafter. The capillary was then broken by twisting the rod R. The levelling tube was re-adjusted and the volume read off, the temperature and barometric pressure being noted at the same time.

In the case of liquids boiling above 100°, the outer jacket was filled with the vapour of boiling decahydronaphthalene.

The results given in the following tables show good agreement with the values required by theory, while there is a considerable economy effected in the time required for the experiment. The compact size of the apparatus facilitates the maintenance of a uniform temperature. The liquid in the capillary, being already heated above its boiling point, vaporises instantaneously on breaking the tube. As the volume can be read off quickly, errors due to diffusion and other accidental causes are reduced to a minimum.

TABLE I.

Chloroform.

Theoretical mol. wt. = 118·4.

Wt. of liquid (mg.).	Temp.	Press. (mm.).	Vol. of air displaced (c. c.).	Mol. wt.
14·3	31·5	759·2	2·99	119·6
8·00	31·5	,,	1·69	118·4
16·2	32·0	,,	3·44	118·0
11·7	28·2	762·0	2·40	120·1
19·9	30·2	760·0	4·07	121·6

TABLE II.

Carbon tetrachloride.

Theoretical mol. wt.=153·84.

Wt. of liquid (mg.).	Temp.	Press. (mm.).	Vol. of air displaced (c. c.).	Mol. wt.
17·9	31·3	758·3	2·88	155·6
21·3	31·5	759·0	3·39	157·2
19·9	32·0	,,	3·17	157·1
25·8	30·2	760·0	4·05	155·3
15·7	31·0	,,	2·51	156·1

TABLE III.

Methyl alcohol.

Theoretical mol. wt.=32·03.

2·27	31·5	758·0	1·76	32·31
4·10	31·3	758·0	3·18	32·80
4·96	31·6	761·0	4·03	30·73
3·46	31·0	760·0	2·74	31·50
4·85	31·0	,,	3·74	32·34

TABLE IV.

Acetone.

Theoretical mol. wt.=58·05.

5·60	31·5	759·4	2·40	58·37
8·80	31·3	759·0	3·78	58·22
5·08	31·3	758·3	2·23	57·02
3·08	30·6	760·0	1·35	56·84
3·81	30·6	,,	1·65	57·51

TABLE V.

Chlorobenzene.

Theoretical mol. wt. = 112·5.

Wt. of liquid (mg.).	Temp.	Press. (mm.).	Vol. of air displaced (c. c.).	Mol. wt.
7·90	31·8	758·0	1·72	115·2
14·4	33·1	759·5	3·09	117·1
15·0	33·0	761·0	3·36	111·9
14·7	32·3	758·0	3·24	114·0
12·7	32·2	,,	2·83	112·7

Our thanks are due to Professor B. B. Dey, for his helpful suggestions.

PRESIDENCY COLLEGE,
MADRAS.

Received August 7, 1931.

Studies in the Acenaphthenequinone Series.

By Anukul Chandra Sircar and Sailesh Chandra Sen.

The present investigation is a continuation of the work of Sircar and Guha Roy (*J. Chem. Soc.*, 1925, **127**, 1048; 1929, **6**, 93) and undertaken with the object of making a further and thorough study of the various reactions of acenaphthenequinone which are comparable to those of phenanthraquinone.

Sircar and Guha Roy (*J. Chem. Soc.*, 1925, **127**, 1048) have already shown that contrary to the conclusions of Japp and his co-workers (*J. Chem. Soc.*, 1882, **41**, 146), the same aldehyde can be made to react with phenanthraquinone in presence of ammonia under different experimental conditions of temperature and pressure to yield either an oxazole or an iminazole.

Though Sircar and Guha Roy (*J. Indian Chem. Soc.*, 1929, **6**, 93) prepared a number of oxazoles and iminazoles by the condensation of aromatic aldehydes with acenaphthenequinone in presence of ammonia, they failed to prepare both oxazole and iminazole by the action of the same aldehyde on acenaphthenequinone.

The authors have now found that:—

A. With (1) *p*-chlorobenzaldehyde, (2) *p*-acetylaminobenzaldehyde, (3) *o*-nitrobenzaldehyde, (4) *p*-dimethylamidobenzaldehyde and (5) resorcylaldehyde at the ice-cold temperature, only oxazoles are formed, but at higher temperature only iminazoles and no oxazales are formed.

B. When (1) *o*-chlorobenzaldehyde, (2) salicylaldehyde and (3) *m*-hydroxybenzaldehyde are condensed with acenaphthenequinone at the ice-cold temperature in presence of ammonia, invariably a mixture of oxazoles and iminazoles is formed as is evident from their percentage compositions. They cannot however be separated from each other owing to their very little and similar solubilities in most of the organic solvents. But if the reaction is brought about at a higher temperature, then only iminazoles and no oxazoles are obtained.

C. With (1) *p*-nitrobenzaldehyde (2) *p*-hydroxybenzaldehyde and (3) anisylaldehyde even at the ice-cold temperature, only iminazoles and no oxazoles are formed.

D. With (1) vanillin and (2) *p*-bromosalicylaldehyde scarcely any reaction takes place at ice-cold temperature, whereas at higher temperature iminazoles are formed as usual.

From the above results one would be naturally inclined to assume that if the reactions could be carried with the aldehydes under the groups B and C, at a still lower temperature, oxazoles might probably have been obtained without the admixture of any iminazole and probably the oxazoles will be formed at some intermediate temperature with the two aldehydes under the group D, and this still remains to be investigated.

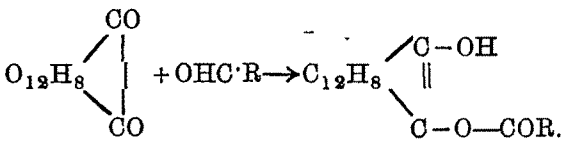
It is interesting to note that only in the case of the *para* substituted aldehydes, if the condensations are effected at a still higher temperature and in a sealed tube, a third and a new type of compound is formed. The percentage of nitrogen in them are almost exactly one and half times of that required by the corresponding iminazoles. They are also deeper in colour than the corresponding iminazoles but nothing definite can be said about their constitution without further study.

The formation of both oxazoles and iminazoles by the condensation of the same aldehyde with acenaphthenequinone in presence of ammonia naturally leads one to suppose that most probably in these reactions oxazoles are first formed which, by subsequent replacement of the oxygen atom of the ring by -NH- group results in the formation of iminazole. Such a replacement is not uncommon, *e.g.*, when pyrones and allied compounds are digested with ammonia, pyridones are formed. (*cf.* Ruhemann, *J. Chem. Soc.*, 1899, **75**, 413; also Meyer and Oppelt, *Ber.*, 1888, **21**, 3376).

In order to test how far this supposition is justified an attempt was made to prepare iminazole by heating the corresponding oxazole with ammonia in a sealed tube under pressure. Though the expected iminazole could not be obtained in a pure state in that way, it is interesting to find that the percentage of nitrogen in the resulting product appreciably increased. Evidently at least a partial conversion of the oxazole to iminazole has taken place. Experiments at still higher temperature and pressure are being undertaken by one of us (A.C.S.).

Klinger and Roerdansz (*Annalen*, 1911, **382**, 211) studied the

action of sunlight on mixtures of various aldehydes and phenanthraquinone in presence of benzene and obtained interesting addition products of the following type

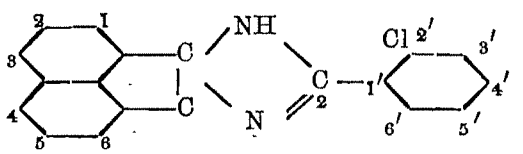


In a similar way acenaphthenequinone has been condensed in presence of sunlight with (1) salicylaldehyde, (2) cinnamicaldehyde, (3) benzaldehyde and (4) anisaldehyde, and the results obtained are exactly alike to those of Klinger and Roerdansz (*loc. cit.*).

Adopting the method of Japp and Miller (*J. Chem. Soc.*, 1885, 47, 11), who were able to condense phenanthraquinone with acetone, monoacetoneacenaphthenequinone has been obtained. The corresponding diacetone derivative could not however be isolated in a sufficiently pure condition.

Experimental.*

2′-Chloro-2-phenylacenaphthiminazole.



Acenaphthenequinone (1 g.) was thoroughly mixed with little more than the molecular proportion of *o*-chlorobenzldehyde and dissolved in about 90 c.c. of boiling amyl alcohol. Dry ammonia gas was then passed through the hot solution for about two hours and the solution left over night. The separated red precipitate, after being thoroughly washed with ether, was crystallised from a mixture of alcohol and toluene as red needles, not melting below 290°.

It dissolves in concentrated sulphuric acid with a red coloration. It is soluble in nitrobenzene, pyridine or acetic acid, sparingly soluble in alcohol, acetone or benzene and insoluble in ether. It dyes wool in light orange shades from an acetic acid bath. (Found: N, 8·9. $C_{19}H_{11}N_2Cl$ requires N, 9·27 per cent.).

* Of the oxazoles and iminazoles mentioned in the paper, those that had already been prepared by Sircar and Guha Roy (*loc. cit.*) have not been described.

The acenaphthiminazoles described in Table I were prepared in a similar way and possess properties similar to the preceding compound. The dyeings were made from an acetic acid bath.

TABLE I

Name of product. (P = 2-phenylacenaphthiminazole)	Formula.	Appearance.	Shade on wool.	Analysis. Found.	Calc.
4′-Chloro-P*	$C_{19}H_{11}N_2Cl$	Shining red needles from a mixture of alcohol and toluene.	Pink.	N, 9·5	9·27 p.c
3′-Hydroxy-P	$C_{19}H_{12}ON_2$	Shining red needles.	Orange.	N, 10·2	9·86 ,,
2′-Hydroxy-4′-bromo-P	$C_{19}H_{11}ON_2Br$	Deep red microcrystalline powder from hot pyridine by cautious addition of hot water.	Yellowish-orange.	N, 7·9	7·7 ,,
3-Nitro-4′-acetylamino-P**	$C_{21}H_{14}N_4O_3$	Deep chocolate coloured microcrystalline powder from hot nitrobenzene by precipitation with ether.	Greenish brown.	N, 14·8	15·13 ,,
3 :4-Dinitro-4′-acetylamino-P	$C_{21}H_{13}N_5O_5$	Do	Scarlet-red.	N, 16·6	16·86 ,,
3-Nitro-4′-chloro-P	$C_{19}H_{10}O_2N_3Cl$	Do	Greyish yellow.	N, 11·80	12·10
3-nitro 4′-hydroxy-3′-methoxy-P	$C_{20}H_{13}O_4N_3$	Dark chocolate coloured powder from hot pyridine by addition of hot water.	Chocolate brown.	N, 11·8	11·69 ,,

* This compound had been prepared by Sircar and Guha Roy (*loc. cit.*). They describe it as rose-coloured rectangular plates (from pyridine), melting at 264° with previous shrinking at 242°. Other properties agree.

** The 3 nitro-and 3 :4-dinitroacenaphthenequinones used in this investigation were prepared according to the methods of Mayer and Kaufmann (*Ber.*, 1920, 53, 269) and Rowe and Davies (*J. Chem. Soc.*, 1920. 117, 1347) respectively.

3′ : 5′-Dihydroxy-2-phenylacenaphthiminazole.—Through a solution of an intimate mixture of resorcylaldehyde (1 g.) and acenaphthenequinone (1 g.) in 300 c.c. of boiling alcohol, dry ammonia gas was passed for two hours and the mixture allowed to stand for seven days, when a dark chocolate coloured solid gradually separated. This was filtered off and crystallised from a mixture of benzene and alcohol as rectangular plates or prisms.

It is sparingly soluble in alcohol or acetone, moderately soluble in toluene and soluble in acetic acid or pyridine. It dissolves in concentrated sulphuric acid with a red colour and a violetish fluorescence. It does not melt below 300°. It dyes wool in yellowish brown shades. (Found: N, 9·2. $C_{19}H_{12}O_2N_2$ requires N, 9·33 per cent.).

4′-Hydroxy-3′-methoxy-2-phenylacenaphthiminzole was prepared in a similar way and possesses properties similar to the preceding compound (shining red needles). It dyes wool in pink shades. (Found: N, 8·6. $C_{20}H_{14}O_2N_2$ requires N, 8·92 per cent.).

2′-Nitro-2-phenylacenaphthiminazole.—Acenaphthenequinone (1g.) was thoroughly mixed with nitrobenzaldehyde (1 g.) and heated in a sealed tube with liq. ammonia for about one hour without using any solvent at 80-100°.

The resulting solid was thoroughly washed with ether and finally purified from a mixture of alcohol and benzene. It is a greyish microcrystalline powder, melting at 150° with decomposition.

It is soluble in toluene, benzene, acetic acid or pyridine and insoluble in ether. It dyes wool in brownish-yellow shades. (Found: N, 13·9. $C_{19}H_{11}O_2N_3$ requires N, 13·42 per cent.).

The following two iminazoles were prepared in the same way as and possess properties similar to the preceding compound.

4′-Acetylamino-2-phenylacenapthiminazole is yellow microcrystalline powder, melts at 255° with decomposition and dyes wool in yellow shades. (Found: N, 13·2. $C_{21}H_{15}ON_3$ requires N, 12·92 per cent.).

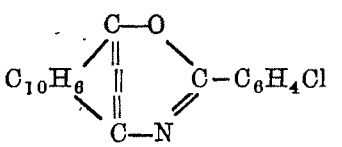
4′-Dimethylamino-2-phenylacenaphthiminazole is deep red microcrystalline powder, melting at 223° with decomposition. It dyes wool in orange brown shades. (Found: N, 13·8. $C_{21}H_{17}N_3$ requires N, 13·5 per cent.).

4′-Hydroxy-2-phenylacenaphthiminazole—Through a solution of an intimate mixture of acenaphthenequinone (1 g.) and *p*-hydroxybenzaldehyde (1 g.) in 60 c.c. of boiling amyl alcohol, dry ammonia gas was passed for about 5 minutes, by which time the reaction set

in. The mixture was then cooled by a freezing mixture and the passing of ammonia continued for further two hours, after which the mixture was allowed to stand for 4-5 hours when a light orange coloured solid separated. This was filtered off, washed with ether, and crystallished from acetic acid as red needles not melting below 290°. It dissolves in concentrated sulphuric acid with a red colouration. It is soluble in nitrobenzene, and sparingly soluble in toluene. It dyes wool in light orange shades. (Found: N, 10·0. $C_{19}H_{12}O\,N_2$, requires N, 9·86 per cent.).

4'-Nitro-2-phenylacenaphthiminazole was prepared in the same way as the preceding compound and obtained as yellow microcrystalline powder (from nitro benzene), melting at 185° with decomposition. It dyes wool in yellow shades. (Found: N, 13·6. $C_{19}H_{11}ON_3$ requires N, 13·42 per cent.).

4' Chloro-2-phenylacenaphthoxazole.



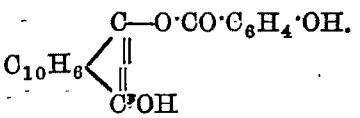
An intimate mixture of acenaphthenequinone (1 g.) and little more than the molecular quantity of *p*-chlorobenzaldehyde was dissolved in boiling amyl alcohol and dry ammonia gas was passed through the hot solution for about 4 minutes. When the reaction had just commenced the mixture was cooled by freezing mixture, ammonia gas was passed for further two hours and then the mixture allowed to stand over night. The light rose-red solid which had separated was filtered off, washed with ether and crystallised from pyridine as rhombic plates mixed with needles, melting at 245° with decomposition. It dissolves in concentrated sulphuric acid with a light red colouration. It is soluble in nitrobenzene and is sparingly soluble in benzene or toluene. It dyes wool in very light rose shades. (Found: N, 4·9. $C_{19}H_{10}ONCl$ requires N, 4·65 per cent.).

4'-Acetylamino-2-phenylacenaphthoxazole was obtained in a similar way as light rose-coloured plates and needles (from pyridine). It is soluble in acetic acid or pyridine, insoluble in ether, acetone or alcohol. It melts at 280° with decomposition. It dyes wool in very light orange shades. (Found: N, 8·2; $C_{21}H_{14}O_2N_2$, requires N, 8·59 per cent.).

Attempt for the conversion of Oxazole to Iminazole.

2′-Nitro-2-phenylacenaphthoxazole was heated in a sealed tube with liquor ammonia for 6 hours in a Carius' furnace (temp. 180°,—above which the tube invariably bursted) and the solid left in the tube crystallised from a mixture of toluene and alcohol. Increase in nitrogen by 0·2 p.c. (in 6 hours), 1·5 p. c. (in 30 hours.) In the case of 4′-acetylamino-2-phenylacenaphthoxazole the increase noted was 2·2 p.c.

Monosalicyloyl derivative of *acenaphthenequinol.*



A mixture of acenaphthenequinone (2 g.), salicylaldehyde (1·2 c.c.) and benzene (12 c.c.) was introduced in a sealed thin glass tube and exposed to bright sunlight for about a month by which time the colour of the quinone completely changed and a blackish mass was obtained. It was treated with a mixture of alcohol and benzene when a part remained undissolved, and a portion went in solution. The insoluble portion was repeatedly crystallised from a mixture of alcohol and benzene and finally obtained as very light yellow needles.

It melts at 192° with decomposition. It is decomposed when treated with alkali and develops a bluish coloration. (Found: C, 74·6; H, 4·4. $C_{19}H_{12}O_4$ requires C, 75·0 ; H, 3·9 per cent.).

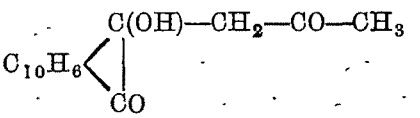
The compound yields an acetyl derivative m. p. 248°.

Similar condensation products with other aldehydes are detailed in Table II.

TABLE II.

Aldehyde taken.	Period of exposure to sunlight.	Appearance & M.P.	Analysis Found.	Calc.
Cinnamicaldehyde	40 days	Yellowish microcrystalline powder, melting at 246° with decomposition.	C, 79·2 H, 3·9	80·2 p.c. 4·45
Benzaldehyde	15 days	Grey coloured microcrystalline powder, melting at 230° with decomposition.	C, 78·6 H, 3·5	79·16 4·16
Anisaldehyde	20 days	M.P. 193° with decomposition..	C, 74·6 H, 5·0	75·47 4·4

Monoacetonéacenaphthenequinone.



A mixture of acenaphthenquinone (5 g.) and acetone (4·5 g.) was treated with 0·25 c.c. of caustic potash solution (*d* 1·27) and the mixture thoroughly shaken. A reaction soon set in, the mass blackened with the rise of temperature. After about ten minutes, the black viscous mass was exposed to air, when it changed to a hard solid. This was triturated with ether and kept for about 4-5 hours. The yellowish precipitate was filtered off, the filtrate (A) kept aside. The former was further washed with ether till the ethereal solution was colourless, and repeatedly crystallised from acetone (bright yellow needles). It melts at 252° and its chemical properties respond to those of acenaphthenequinone.

The coloured ethereal solution (A) was treated with animal charcoal and filtered, when the solution became almost colourless. The tarry mass which separated on evaporation of the ether was crystallised from a mixture of alcohol and ether in colourless needles, melting at 117° with decomposition. It is soluble in almost all organic solvents. (Found: C, 74·5; H, 5·3. $C_{15}H_{12}O_3$ requires C, 75·0 ; H, 5·0 per cent.).

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Received August 25, 1931.

Interaction between Copper Oxide and Neutral Salt Solutions.

By M. P. Venkatarama Iyer.

In a previous communication (Mukherjee and Iyer, *J. Indian Chem. Soc.*, 1926, 3, 307), the nature of the interface between copper oxide and the aqueous phase as deduced from electro-osmotic measurements was briefly discussed and conclusions were drawn from the experimental data regarding the interchange of ions between the double layer and the aqueous phase. The investigation of the reaction between systems like copper oxide and neutral salts is very interesting, in so far as such reactions can be interpreted from the two rival points of view. Mukherjee (*Presidential Address, Indian Science Congress*, 1929) has pointed out clearly experiments which decide definitely in favour of the Ion Adsorption Theory. The various physical and chemical properties of *interfaces* can be always determined by the nature of the *fixation* of ions at the interface. The variation of the electrical charge of copper oxide in contact with solutions of salts has been discussed in the previous paper (*loc. cit.*). In the present paper, the adsorption and liberation of alkali by copper oxide has been undertaken and the nature of the ion-exchanges taking place has been fully elucidated and the defects of the 'Chemical Theory' pointed out.

Experimental.

The purity of the sample of the copper oxide is of extreme importance in investigations of this type, where the amount of alkali liberated is of the order of 10^{-6} g. ions and hence very great care was taken in the preparation of the copper oxide. It was obtained by treating copper sulphate solution with a slight excess of sodium hydroxide in the hot condition and the precipitate was then washed for several days by decantation. When the sample as tested with the wash liquid was fairly free from alkali, it was subsequently subjected to a process of electro-dialysis using collodion membrane and

a 110 volt D.C. Conductivity water was employed for the purification of the substance. The purity of the substance finally obtained was found out by determining whether the conductivity of the wash liquid was identical with that of the water employed for washing. It was noticed that as the process of purification proceeded, the substance passed into the colloidal condition. The sample was finally dried in an air oven at 100°.

(A) *Liberation of alkali with electrolytes.*—The experimental technique employed for the measurement of alkalinity is much the same as that elaborated by Mukherjee and co-workers. (*cf. J. Chem. Soc.*, 1926, **128**, 3023; Ghosh, *J. Chem. Soc.*, 1926, **128**, 2605). Care was taken to see that the alkalinity developed was not due to the solution of the glass, by performing blank experiments in similar Jena vessels.

TABLE I.

Alkali liberated with different electrolytes.

Copper oxide in contact with	pH.		pH.
(*a*) Pure water ...	6·6	(*f*) *N*-$BaCl_2$ ...	9·4
(*b*) *N*-KCl ...	9·4	(*g*) ·1 *N*-$BaCl_2$ ...	9·1
(*c*) ·1 *N*-KCl ...	9·0	(*h*) *N*-K_2SO_4 ...	9·8
(*d*) *N*-NaCl. ...	9·4	(*i*) *N*-Na_2SO_4	9·8
(*e*) ·1 *N*-NaCl. ...	9·0	(*j*) *N*-KNO_3 ...	9·2
		(*k*) ·1 *N*-KNO_3 ...	9·0

It can be clearly seen from the above that there is a very close correlation between the development of alkali and the electrokinetic behaviour of the substance, as deduced from electro-omotic measurements cited in the previous paper. Two points are brought out very clearly.

(1) The nature of the cation employed has little influence on the amount of alkali liberated.

(2) The valency of the anion determines the alkalinity developed and follows the series $SO_4''>Cl'>NO_3'$.

(B) *Measurements of the alkali liberated from the sample of copper oxide.*—A known weight (10 g.) of the sample was taken in a Jena bottle and shaken up with 100 c.c. of *N*-KCl solution and

allowed to stand for 24 hours. The alkalinity developed was measured and after pipetting out carefully most of the supernatant liquid, another 100 c.c. of *N*-KCl was added and the same process was repeated from day to day. The following table gives the values obtained:—

TABLE II.

Total alkali liberated from copper oxide.

Copper oxide taken = 10 g. Vol of *N*-KCl added = 100 c.c.

Day.	p_H of supernatant liquid.	Day.	p_H of supernatant liquid.
1st.	9·4	12th.	8·4
2nd.	9·4	13th.	8·2
3rd.	9·3	14th.	8·0
4th.	9·2	15th.	7·8
5th.	9·0	16th.	7·7
6th.	9·1	17th.	7·6
7th.	9·05	18th.	7·6
8th.	9·0	19th.	7·6
9th.	8·9	20th.	7·6
10th.	8·8	20th.—30th.	7·6 each day
11th.	8·6		

From the above data, the total alkali liberated from one gram of copper oxide is found to be equal to $1{\cdot}3904 \times 10^{-6}$ g. ions per gram of the copper oxide.

The day-to-day measurement of the p^H of the liquid offers a very interesting evidence regarding the interchange of ions that takes place in the double layer as is pointed out in the discussion. It is also noticed that the colour of the precipitate changes appreciably during the final stages of the washing with KCl. Originally the copper oxide is dark in colour, but as the washing with potassium chloride proceeds, it gets a greenish tinge. Since the constant p_H of 7·6 was maintained for several days, and there was no indication of any fall in its value, attempts were made to find out the effect of washing the sample with water at this stage and it

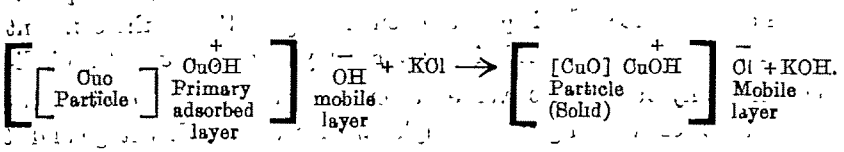
was found that the p_H of the wash water was 6·2 for the first washing with 100 c.c. of water and 6·0 for the next 100 c.c. The washing was thus continued and considerable amounts of acid was thus liberated until finally the substance got back to the original colloidal condition, when the p_H also reached 6·8. Again the same process of liberation of alkali with neutral salts could be repeated.

(C) *Adsorption of alkalies by copper oxide.*—Experiments were performed to find out if the sample of pure copper oxide is capable of adsorbing alkali. The method adopted was based on the loss of conductivity of a very dilute solution of sodium or barium hydroxide, when it was shaken up with a given quantity of copper oxide. Allowance was made for the dilution which might be introduced by the moisture contained in the copper oxide. It is found that there is a distinct loss of conductance when the sample is shaken up with alkali. The amount of alkali adsorbed per g. of the sample $= 1{\cdot}12 \times 10^{-6}$ g. ions. per gram of CuO.

Discussion.

In the previous paper (*loc. cit.*), it was suggested that the ions in primary layer must be assumed to be univalent, *i.e.*, cupric ions with a fixed hydroxyl ion forming the univalent positive unit, and hydroxyl ions equal in number forming the mobile sheet of the double layer. It is observed that the alkalinity developed is determined by the concentration of the electrolyte also, which is to be expected on the basis of the Ion Adsorption Theory.

The case of copper oxide, for which there is distinct evidence to show that it is dehydrated, differs from that of silica which is heavily hydrated. We may picture the interface, in the case of CuO, as consisting of solid particles on which, according to the views of Mukherjee, an excess of CuOH ions are fixed at certain points due to the operation of chemical valency forces and OH ions which go to form the mobile sheet of the double layer. According to this view, the formation of alkali may be represented by the reaction.



Thus the maximum amount of alkali liberated in the primary stage is determined by the number of hydroxyl ions in the mobile sheet of the double layer. Besides this primary reaction, a secondary one resulting in the replacement of a certain number $CuOH^+$ by $CuCl^+$ is possible and this would result in the net positive charge being increased. It should be noted that the replacement of OH in the primary layer is not so easy as in the secondary layer and is a slow process. This explains the constant p_H of 7·6 which continues for days together. The change in colour pointed out earlier is according to the ' Chemical Theory' due to the basic chloride being formed at the interface. The development of the acidity when the sample is treated with water can be represented by the reaction:

$$\left[\underset{\text{Solid}}{[CuO]}\ CuOH^+\right]\ \bar{Cl} + H_2O \rightarrow \left[\underset{\text{Solid}}{CuO}\ CuOH^+\right]\ OH^- + HCl$$

This explains the experimental result that we get back the original sample on repeatedly washing the above sample with water.

If we try to explain the liberation of alkali and the electrokinetic behaviour of copper oxide with potassium sulphate solution, we have to assume a series of chemical changes of the following type to take place as has been discussed by Mukherjee. (*i*) " At low concentrations, ' complex ' cations containing alkali metal ions are formed such that the product of the free valencies and the additional complex ions is greater than that of the original non-diffusible ions, whose place they have taken or that the more dissociable copper sulphate molecules are formed on the surface." (*ii*) In the second place, the undissociated molecules of copper sulphate are formed resulting in the diminution of charge and liberation of alkali. (*iii*) At still higher concentrations we have to assume the formation of some complexes which get negatively charged. Simultaneously with the formation of basic anion, it is necessary to assume that the basic sulphate is also formed. When the concentration is still further increased, the degree of dissociation of the complex must still further diminish. Thus the ' Chemical Theory ' imposes too many arbitrary assumptions and it is also difficult to see why the complexes remain fixed on the surface and why they are so readily formed with polyvalent ions of opposite sign. Then again, it is necessary to make suitable assumptions regarding

the solubility of these complexes. The difference between the "Chemical Theory' and the 'Adsorption Theory' pointed herein, is that the chemical reactions, if they take place at all, must be confined in cases of this type to the surface layer and as such there cannot be any stoichiometric relationship.

Summary.

1. The liberation of alkali when highly purified copper oxide is shaken up with neutral salt solutions is closely connected with the electrokinetic behaviour of the substance in contact with solutions of different electrolytes. Just as the valency and mobility of the 'anion' of the added electrolyte determines the electrical charge on the particles, so also the concentration of alkali liberated depends on the nature and concentration of the anion and not the cation.

2. The *primary* adsorption of hydroxyl ions by the sample of copper oxide has been proved by conductivity measurements.

3. The total quantity of alkali liberated from a given amount of the copper oxide by neutral salt solutions bears no stoichiometric relationship to the amount of substance taken.

4. The *Surface Dissociation Theory*, when applied to the system, Cuo-neutral salt solutions, is found to be untenable, since it involves making too many arbitrary assumptions, while the *Adsorption Theory*, as put forward by Mukherjee, can explain the different sets of phenomena in a very satisfactory way.

The author wishes to thank Prof. B. Sanjiva Rao for the facilities he provided.

CHEMISTRY DEPARTMENT,
CENTRAL COLLEGE, BANGALORE.

Received September 9, 1931.

Synthesis of Coumarins and Chromones.

A Preliminary Note.

By Dukkhaharan Chakravarti.

It has been shown by the author (*J. Indian Chem. Soc.*, 1931, 8, 129, 407) that Simoni's method of synthesis of chromones from phenols and β-ketonic esters using phosphorus pentoxide as the condensing agent is not of general application and that polyhydroxy phenols, *viz.*, resorcinol, orcinol, pyrogallol, phloroglucinol, as also α-napthol give coumarins even with phosphorus pentoxide. Further investigations in this direction show that only those phenols, which react with difficulty or do not react at all with β-ketonic esters using sulphuric acid to form coumarins, yield with phosphorus pentoxide chromones; while those phenols which form coumarins readily with good yield using sulphuric acid, invariably give coumarins by changing the condensing agent for phosphorus pentoxide. Thus phenol, cresols, β-naphthol, halogenated phenols, nitrophenols and phenol-carboxylic acids, guiacol and hydroquinone yield always chromones, when condensed with substituted ethyl acetoacetates (the substituents being methyl, ethyl, propyl, *iso*propyl, allyl, *iso*butyl, benzyl amyl and chloro), the yield increasing as the substituents become heavier. As these chromones contain a reactive methyl group in 2-position, they readily react with benzaldehyde to form styrene derivatives, and they are thus distinguished from the isomeric coumarins. In order to find a satisfactory explanation of the mechanism of this reaction, the condensations of resorcinol-mono- and dimethyl-ether with ethyl acetoacetates and with ethyldimethyl- (or diethyl)-acetoacetate have also been attempted in the presence of sulphuric acid or phosphorus pentoxide with interesting results. The details of this investigation will be communicated as soon as the analytical work is finished.

...AL LABORATORY,
...CALCUTTA.

Received October 6, 1931.

A paper entitled " Synthesis of Coumarins from Phenols and ketonic Esters using Phosphorus Pentoxide. Part I. Coumarins from Resorcinol and Ethylacetoacetates " was submitted to the Indian Chemical Society by the author, D. Chakravarti, on the 9th February, 1931 ; whereas work on similar lines seems to have been carried on by Robertson and his collaborators, at the London School of Hygiene and Tropical Medicine and was submitted for publication to the Chemical Society, London, on the 16th March, 1931.

Since then, both Chakravarti and Robertson are simultaneously working in India and England on the same lines and are publishing their work in the Journals of the Indian Chemical Society, Calcutta (India) and the Chemical Society, London, respectively.

Editor.

An Analogue of the Acclimatisation Phenomenon in the Protection of Arsenious Sulphide Sol by Gelatine.

By A. Joga Rao.

In connection with a study of the coagulation of colloids in the presence of protective agents, to be communicated shortly, the interesting question has arisen about the difference in the stability of a sol produced by a variation in the manner of addition of the protective agent. Since no information on this point is to be found in the literature, it is intended in this note to record results of some preliminary observations which served to indicate this possibility.

Ten c.c. of a stock solution of arsenious sulphide sol were taken in two similar flasks. An equal volume of a 0·05% gelatine solution was added to each. In one set of observations the gelatine was introduced by a single addition and the resulting mixture shaken, whilst in the other, the same volume from the same gelatine solution was added in about twenty instalments, the mixture being shaken similarly after each addition; the two sets of mixtures were then allowed to stand for about 24 hrs. and then equi-coagulating concentrations of a dilute barium chloride solution were determined with the sols. This quantity as a result of ten independent observations on each system was found to be $N/40$ and $N/50$, corresponding to protection by single addition and dropwise addition respectively.

This conclusion was further tested by colorimetric observations. The two limbs of the colorimeter were filled with samples of the two sols and the heights adjusted to equal visibility. One typical set of results is given below:

Single addition	...	25
Drop-wise addition		

These results show th
opacity) is produ
gelatine

is in agreement with the other set of experiments which indicate that the drop-wise addition of the protector corresponds to a lower concentration of the electrolyte solution for producing in the same degree of coagulation. This lower stability of the system might be explained by the following considerations.

It is evident that protection depends upon the adsorption of the protecting agent by the sol. When the introduction of a given amount of the protecting agent is spread over a number of instalments, the resultant of a certain adsorption of the protector by the sol particle might serve as the basis for further adsorption in a subsequent addition and so on. The result is that the net adsorption in the above case, reckoned per colloid particle, is greater than that corresponding to a single addition of the protector. The average size of the particle in the former case would therefore be greater than in the latter and hence the observed difference in coagulability.

Furthermore, it is known that the stability of a particle in a sol is greater, the less the interfacial tension between itself and the immediately contiguous medium. The reduction in this interfacial tension would increase by increasing the concentration of a substance like gelatine, which is an efficient emulsifying agent. This might be another factor in the greater stability of the sol protected by introducing the gelatine solution in a single addition, since the corresponding continuous medium would be richer in gelatine.

It might further be pointed out that there is considerable evidence (Smoluchowski, *Z. Phys. Chem.*, 1917, **92**, 155; Freundlich and Basu, *ibid.*, 1925, **115**, 203) to show that stirring, etc., increase the rate of coagulation, presumably by increasing the frequency of collision (leading to coalescence) amongst the colloid particles. Since in drop-wise addition the system is subjected to a longer (intermittent) period of stirring than in the other case, difference in stability as observed is to be anticipated.

The author wishes to express his sincere thanks to Prof. S. S. Joshi, D.Sc. [illegible] luable suggestions in explaining the obser[illegible]

[illegible]ceived August 10, 1931.

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part XIII. Naphthylene Derivatives of Stereoisomeric Iminocamphors and Methylenecamphors.

By Bawa Kartar Singh and Bhutnath Bhaduri.

In the present communication we give an account of our experiments on the optical rotatory dispersion of the condensation products of camphorquinones (*d*, *l*, *dl*) and oxymethylenecamphors (*d*, *l*, *dl*) with naphthylenediamines (1:2 and 1:5).

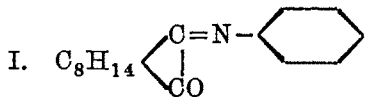
1.2-Benzocamphanoquinoxalines (*d*, *l*) prepared by us melts at 116-17° and the *racemic* form at 123-24° (*vide* Experimental). Heckendorn (*Helv. Chim. Acta*, 1929, **12**, 60) records 85-86° as the melting point of the *dextro* compound. Our repeated attempts to isolate a compound having this low melting point have failed and in the absence of any experimental data we provisionally assume it to be a dimorphous form of the compound prepared by us; but as no data of rotatory power are given by Heckendorn, for the lower melting compound, it is not possible for us to give a definite opinion on this point.

The condensation products of oxymethylenecamphors (*d*, *l*, *dl*) with 1:2-naphthylenediamine are oils which refused to solidify. The condensation products of camphorquinones (*d*, *l*, *dl*) with 1:5-naphthylenediamine consist of two different types of compounds, *viz.*, 1:5-naphthylenebisiminocamphor (VII) and 1-amino-5-naphthyliminocamphor (X) which can be separated by fractional crystallisation (*vide* Experimental).

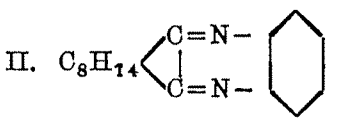
Compounds described in the paper have been examined with a view to find the effect of (1) chemical constitution and (2) nature of solvent on the rotatory power and the results are as follows.

(1) The effect of a ring structure on rotatory power is very well brought out by comparing the structural formulae of phenyliminocamphor (I) and α-naphthyliminocamphor (III) with those of camphanoquinoxaline (II) prepared by Singh and Majumdar (*J. Chem.*

Soc., 1919, **115**, 566) and 1:2-benzocamphanoquinoxalines (IV) respectively.



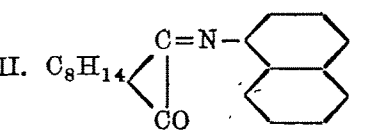
I. C_8H_{14} (C=N– / CO) fused with benzene



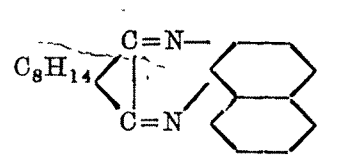
II. C_8H_{14} (C=N– / C=N–) fused with benzene

$[\alpha]_D = +726{\cdot}6°$ (chloroform). $[\alpha]_D = +28{\cdot}5°$ (chloroform).

(Forster and Thornley, *J. Chem. Soc.*, 1909, **95**, 944).



III. C_8H_{14} (C=N– / CO) fused with naphthalene



IV. C_8H_{14} (C=N– / C=N) fused with naphthalene

$[\alpha]_D = +609{\cdot}6°$ (chloroform). $[\alpha]_D = -29°$ (chloroform).

(Singh and Mazumdar, *loc. cit.*).

The doubly linked oxygen atom of the carbonyl group in the aryl derivatives of iminocamphor is replaced by a doubly linked nitrogen atom of the azethenoid group with the ring closure in the *ortho* position in the quinoxaline derivatives. This change in structure (I→II; III→IV) has produced phenomenal depression in the rotatory power of camphanoquinoxaline and in the case of 1:2-benzocamphanoquinoxalines even the sign of the rotatory power has changed. Other cases of depression of rotatory power on ring formation have already been noticed by one of us (Singh and Biswas, *J. Chem. Soc.*, 1924, **125**, 1895; Singh and Puri, *ibid*, 1926, p. 504) for the aryl derivatives of camphoramic acids and camphorimide; *e.g.*, the following are the values of $[M]_D$ in ethyl alcohol; camphorbenzylamic acid (99·88°)→ camphorbenzylimide (30·19°); camphor-*m*-nitrobenzylamic acid (106·7°)→camphor-*m*-nitrobenzylimide (31·92°); camphor-β-naphthylamic acid (229°)→camphor-β-naphthylimide (60°). Again the rotatory powers of esters of 1-methyl-3-*cyclo*pentanone-4-carboxylic acid are about 30 times as great as those of the corresponding esters of methyladipic (Haller, *Compt. rend.*, 1905, **140**, 1205) and the hexahydrophthalic acids have much lower rotatory power than their anhydrides (Werner, *Ber.*, 1899, **32**, 3046). This is even more strinkingly illustrated in the case of monosaccharides.

The rotatory power of *d*-mannitol is $[\alpha]_D^{20°} = -0{\cdot}2°$ (Fischer, *Ber.*, 1890, **23**, 3684) wheras that of *d*-mannonolactone is $+53{\cdot}8°$ (Fischer, *Ber.*, 1889, **22**, 3219). The high rotatory power of most of the sugars as compared with the corresponding polyhydric alcohol is a proof of the ring structure of the former. The increase which is brought about in the rotatory power of sugar alcohols by boric acid is attributed to the formation of ring complexes.

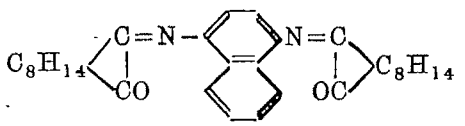
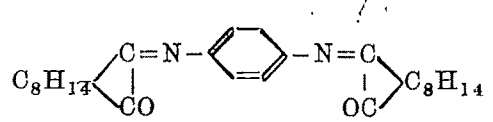
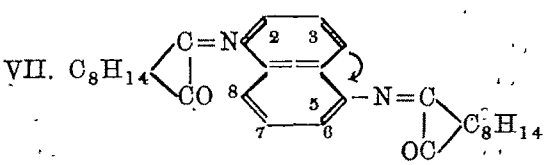
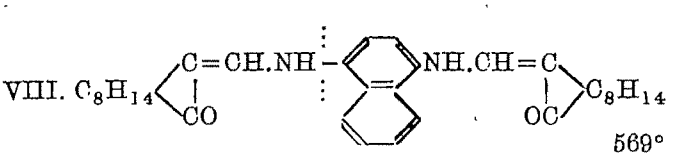
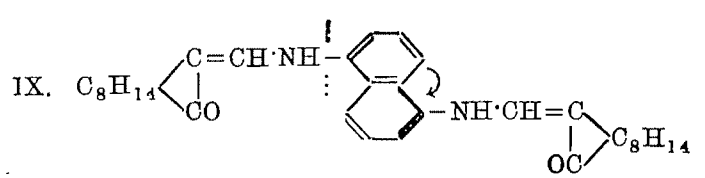
It is thus possible to infer from these and other examples that the rotatory power of a cyclic compound is usually very considerably different from that of the corresponding open chain derivative. It may be greater or less. It is also seen from these examples that the increase or decrease in the rotatory power resulting from ring formation cannot be correlated with the fact that the asymmetric centre lies *within* or *without* this ring.

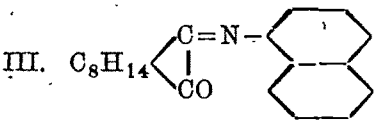
The rotatory power of 1:5-naphthylenebisiminocamphor (VII) is considerably less than one half the value of the rotatory power of the 1:4 compound (V). It is nearly one half the value of *p*-phenylenebisiminocamphor (VI). The low value of the rotatory power of 1:5-naphthylenebisiminocamphor is due to the fact that the conjugation between the carbonyl, azethenoid groups and the naphthalene ring is broken at the *fifth* carbon atom in the naphthalene nucleus (Table A, VII) whereas these conjugation is complete in the case of 1:4-naphthylenebisiminocamphor, and *p*-phenylenebisiminocamphor. The rotatory power of 1:5-naphthylenebisaminomethylene camphor (IX) is only slightly lower than the corresponding 1:4-compound (VIII). The break in the conjugation at the fifth carbon atom in the naphthalene nucleus being distant from the asymmetric centre has very little effect, the greater effect being produced by another break in the conjugation at the secondary amino group which is near the asymmetric centre, and is present in both the compounds.

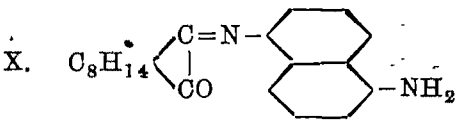
The introduction of an amino-group in the 5-position of α-naphthyliminocamphor (X) lowers the rotation of the parent compound and the acetylation of the amino-group further lowers the same (XI).

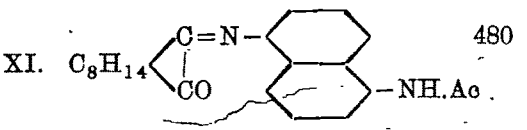
2. The rotatory power of the compounds is higher in pyridine and benzene and lowest in ethyl alcohol and methyl alcohol, which is approximately in the inverse order of the dielectric constants of the solvents.

TABKLE A.

	Structural formula.	$[\alpha]_D$ in chloroform	References
V.		1941°	Sinha & Bhaduri, *J. Indian Chem. Soc.*, 1930, 7, 548.
	(9 conjugated double bonds)		
VI.		1527°	Singh & Bhaduri, *ibid*, p. 548.
	(7 conjugated double bonds).		
VII.		787°	
	(Conjugation broken between the carbon atoms marked 4 & 5 and is shown by the dotted line when counted round the shortest route).		
VIII.		569°	Singh & Bhaduri, *ibid.*, p. 789.
	(conjugated broken at the dotted line).		
IX.		435°	
	(conjugation broken at the dotted lines and arrow).		

III.  609·6° Singh and Majumdar, *J. Chem. Soc.*, 1919, **115**, 573.

X.  565

XI.  480

Except for 1 : 5-naphthylenebisaminomethyleneca mphor the rotatory dispersion for the remaining compounds was studied only for about 8 wave-lengths as the substances were so highly coloured that the lines beyond Hg_{5780} towards the violet end of the visible region of the spectrum could not be viewed through the solution. 1 : 5-Naphthylenebisaminomethylenecamphor, like the other derivatives of oxymethylenecamphors, obeys the simple dispersion equation of Drude, $[\alpha] = \frac{k}{\lambda^2 - \lambda^2_0}$. The values of rotatory power of *d* and *l* forms in different solvents (Tables I-V) are identical within limits of experimental error. Out of 66 observations now recorded, in as many as 47 cases, the difference in the numerical value of specific rotatory power of the opposite isomers corresponds to a difference of less than 0·01° in the observed angle of rotation and in 17 other cases the corresponding angle lies between 0·01° to 0·02° which is the limit of experimental error allowable in such measurements. Only in the remaining 2 cases, *viz.* 1 : 2-benzocamphanoqninoxaline in pyridine for Hg_{violet} and for 1-acetylamino-5-naphthyliminocamphor in pyridine for Na_D (Table IV), the difference corresponds to between 0·02° and 0·03° in the observed angle of rotation. These however, are of the nature of casual experimental errors. This therefore, further supports Pasteur's principle of molecular dissymmetry, according to which the two forms, *dextro* and *laevo*, must possess equal and opposite rotatory power.

Whether a *racemic* form is a *dl*-compound of the *d* and *l* isomers can be sometimes inferred from the melting point determinations.

Three cases may arise: (*a*) The melting point of the *racemic* form is *higher* than that of the active forms, in which case it is a true *dl*-compound, at least in the solid state. The *racemic* form of benzocamphanoquinoxaline is an instance of this nature. (*b*) The melting point of the *racemic* form is lower than that of the opposite active forms, as in the case of 1-amino-5-naphthyliminocamphor. (*c*) The melting point of the *racemic* form is identical with that of the active forms, as in the case of 1:5-naphthylenebisaminomethylenecamphor. In (*b*) and (*c*) other experiments will have to be made before it can be settled whether the *racemic* form is a *dl*-compound or a mixture of the *d* and *l* forms. Examples of *racemic* forms having identical melting points with the active forms are very rare. In our studies we have, up till now, come across only two other instances, namely, camphorquinones (*d*, *l*, *dl*) which melt at 198°-99° and *oo'*-stilbenebisaminomethylenecamphors (*d*, *l*, *dl*), m.p. 295-96° (*J. Indian Chem. Soc.*, 1931, **8**, 190). Other examples which may be cited are:—π monobromocamphor, m.p. 92·4° (Kipping and Pope, *J. Chem. Soc.*, 1895, **97**, 372); limonene-α-nitrosochloride, m p., 103-04° (Wallach. *Annalen*, 859, **111**, 125,252); phenylhydrazide of gulonic acid, m p. 147-49°, and of galactonic acid, m.p. 200-05° (Fischer, *Ber.*, 1894, **27**, 3225); phenylgulosazone, m.p, 157-59° (Fischer. *Ber.*, 1892, **25**, 1030).

Experimental.

1:2-*Benzo*-d-*camphanoquinoxaline*.—*d*-Camphorquinone (1 mol.) in ethyl alcoholic solution was added to the aqueous solution of 1:2-naphthylenediamine hydrochride (1 mol.) and heated in presence of fused sodium acetate at 60° for 45 minutes. The condensed product was extracted with ether and the ethereal solution shaken with concentrated hydrochloric acid sufficient to dissolve the reddish yellow precipitate first formed. The reddish acid layer was separated and diluted with water when a voluminous yellow mass was precipitated. The alcoholic solution was just neutralised with ammonia and crystallised as white prisms melting at 116-17°, yield, 35 p.c. (Found: C, 83·37; H, 6·80; N, 10·00. $C_{20}H_{20}N_2$ requires C, 83·33; H, 6·94 and N, 9·73 per cent.). It is freely soluble in the ordinary organic solvents. *Benzo*-l-*camphanoquinoxaline*, m.p. 116-17°. (Found; N, 9·73. $C_{20}H_{20}N_2$ requires N, 9·73 per cent.). *Benzo*-dl-*camphanoquinoxaline*, m.p. 123-24°. (Found: N, 10·02. $C_{20}H_{20}N_2$ requires N, 9·73 per cent.).

Benzo-d-camphanoquinoxaline could not be reduced even when heated with stannous chloride and hydrochloric acid.

1:5-*Naphthylenebisiminocamphor and* 1-*Amino*-3-*naphthyliminocamphor*.—*d*-Camphorquinone (1·7 g.) was heated with 1:5-naphthylenediamine hydrochloride (2·3 g.) in presence of fused sodium acetate at 99-100° for 8 hours. The condensed product extracted with alcohol contained both the compounds which were separated by fractional crystallisation out of ethyl alcohol in which the bisimino compound is sparingly soluble. First crop, brown amorphous solid, infusible even at 260°, yield, 0·3 g. Second crop: (from the filtrate) after repeated crystallisation from dilute alcohol, yellowish orange crystals (probably prisms) melting at 192-93° were obtained (yield, 1·1 g.).

1:5 *Naphthylenebisimino*-d-*camphor*, infusible even at 260°, fairly easily soluble in chloroform, pyridine, benzene and acetone; sparingly soluble in alcohols (ethyl and methyl) and ether. (Found: N, 6·40. $C_{30}H_{34}O_2N_2$ requires N, 6·17 per cent.).

1-*Amino*-5-*naphthylimino*-d-*camphor*, yellowish orange prisms, m.p. 192-93°, freely soluble in ordinary organic solvents including ether. (Found: C, 78·22; H, 7·37; N, 9·03 and 9·29. $C_{20}H_{22}ON_2$ requires C, 78·43; H, 7·19 and N, 9·15 per cent.).

1:5-*Naphthylenebisimino*-l-*camphor*, infusible even at 260°. (Found: N, 6·25. $C_{30}H_{34}O_2N_2$ requires N, 6·17 per cent.). 1:5-*Naphthylenebisimino*-dl-*camphor*, infusible even at 315°. (Found: N, 6·24. $C_{30}H_{34}O_2N_2$ requires N, 6·17 per cent.).

1-*Amino*-5-*naphthylimino*-l-*camphor*, m.p. 192-93°. (Found: N, 9·40. $C_{20}H_{22}N_2O$ requires N, 9·15 per cent.). 1-*Amino*-5-*naphthylimino*-dl-*camphor*, m.p. 172-73°. (Found: N, 9·36. $C_{20}H_{22}ON_2$ requires N, 9·15 per cent.).

1-*Acetylamino*-5-*naphthylimino*-d-*camphor*.—1-Amino-5-naphthylimino-*d*-camphor was acetylated in the usual way with acetic anhydride and the acetyl compound crystallised out of dilute alcohol as greenish yellow prismatic crystals melting at 173-74°. (Found: C, 75·71; H, 7·13; N, 8·31. $C_{22}H_{24}O_2N_2$ requires C, 75·85; H, 6·90; N, 8·05 per cent.). It is freely soluble in the ordinary organic solvents.

1-*Acetylamino*-5-*naphthylimino*-l-*camphor*, m.p.173°-74°. (Found: C, 75·71; H, 7·14; N, 8·09. $C_{22}H_{24}O_2N_2$ requires C, 75·85; H, 6·90; N, 8·05 per cent.).

1:5-*Naphthylenebisaminomethylene*-d-*camphor*.—Oxymethylene d-camphor (1·8 g.) in methyl alcohol and 1:5-naphthylenediamine-hydrochloride (1·15 g.) in glacial acetic acid with a little fused sodium acetate, were mixed together when a greenish yellow precipitate separated at once. It was crystallised out of pyridine as shining yellow crystals (probably prisms) melting at 322-23°. (Found: C, 79·56; H, 8·08. $C_{32}H_{38}O_2N_2$ requires C, 79·65; H, 7·88 per cent.). It is fairly soluble in chloroform; less so in pyridine and sparingly soluble in benzene, acetone, ether, ethyl alcohol and methyl alcohol.

1:5-*Naphthylenebisaminomethylene*-l-*camphor*, m.p. 322-23°. (Found: N, 5·87. $C_{32}H_{38}O_2N_2$ requires N, 5·81 per cent.). Rotatory power was determined only in chloroform, the substance being sparingly soluble in other solvents. 1:5-*Napthylenebisaminomethylene*-dl-*camphor*, m.p. 322-23°. (Found: N, 5·92. $C_{32}H_{38}O_2N_2$ requires N, 5·81 per cent.).

TABLE I.

1:2-*Benzocamphanoquinoxaline*.

Solvent	Conc. g/100 c.c.	*d*, *l*, or *mean*.	Hg_{violet} [α]	Hg_{gree} [α]	Hg_{yellow} [α]	Na_D [α]
Pyridine	1·0020	*d*	−127·2°	−51·29°	−42 41°	−39·92°
	1·0056	*l*	+125·8	+50·71	+42·26	+39 27
Benzene	1·0040	*d*	−117·9	−46·30	−38·33	−26·33
	1·0012	*l*	+116·9	+46·45	+37·96	+35·96
Chloroform	1·0008	*d*	−91·37	−36·97	−30·48	−28·98
	1·0032	*l*	+92·22	+37·39	+30·40	+29·42
Acetone	1·0040	*d*	−35·36	−13·94	−11·45	−10·46
	1·0008	*l*	+34·47	+13;49	+10·99	+9·99
Ethyl alcolol	1·0008	*d*	−33 98	−13·50	−10·99	−10·00
	1·0036	*l*	+33 40	+12·96	+10·96	+9·47
Methyl alcohol	1·0060	*d*	—	−0·99	−0·49	−0 49

TABLE II.

1:5-*Naphthylenebisiminocamphor.*

Solvent.	Conc. g/100 c.c.	*d*, *l*, or *mean*.	Hg_{yellow} [α]	Na_D [α]
Benzene	0·0516	*d*	+1037·0°	+959·3°
	0 0500	*l*	−1040·0	−960.0
Pyridine	0·0500	*d*	+940·0	+880·0
	0 0512	*l*	−937·6	−878·8
Acetone	0 0516	*d*	+930·3	+872·0
	0 0504	*l*	−922·6	−868·0
Chloroform	0 0540	*d*	+78·70	+740·9
	0 0516	*l*	−794·5	−736·4

Hg_{green} line was very indistinct when viewed through these solutions Rotations in alcohols (ethyl and methyl) could not be obtained as the substance was very difficuity soluble in them.

TABLE III.

1-*Amino-5-naphthyliminocamphor.*

Solvent	Conc. g/100 c.c.	*d*, *l*, or *mean*.	Hg_{yellow} [α]	Na_D [α]
Pyridine	0·1000	*d*	+725·0°	+675·0°
	0 1016	*l*	−728·5	−669·2
Benzene	0·1008	*d*	+689 5	+644·8
	0·1020	*l*	−686·3	−642·2
Acetone	0·1016	*d*	+640·7	+600·5
	0 0996	*l*	−652·5	−602·4
Chloroform	0 1000	*d*	+600·0	+565·0
	0·1008	*l*	−595·3	−560 6
Ethyl alcohol	0·1004	*d*	+597 5	+562·7
	0·1000	*l*	−600 0	−560·0
Methyl alcohol	0 1004	*d*	+577·7	+542·8
	0 1000	*l*	−575·0	−540·0

Hg_{green} line was very indistinct when viewed through most of these solutions; through others it was not at all visible.

TABLE IV.

1-Acetylamino-5-napthyliminocamphor.

Solvent.	Conc. g/100 c.c.	*d*, *l*, or *mean*.	Hg_{green} [α]	Hg_{yellow} [α]	Na_D [α]
Pyridine	0·2008	*d*	+814·4°	+635·0°	+602·7°
	0·2000	*l*	−810 0	−630·0	−597·5
Benzene	0·2000	*d*	+802·5	+622·5	+587·5
	0·2012	*l*	−802·8	−623·8	−586·5
Acetone	0·2012	*d*	+653·8	+519·4	+492·0
	0·2000	*l*	−652·5	−517·5	−487·5
Chloroform	0·2000	*d*	+637·5	+507·5	+480·0
	0·2020	*l*	−636·0	−507·7	−482·6
Ethyl alcohol	0·2008	*d*	+597·7	+478·2	+450·8
	0·2024	*l*	−600 2	−479·2	−454 4
Methyl alcohol	0·2000	*d*	+557·5	+440·0	+416·8
	0·2020	*l*	−559·4	−443·1	−420·7

TABLE V.

1:5-Naphthylenebisaminomethylenecamphor in chloroform.

$$[\alpha] = \pm \frac{79{\cdot}47}{\lambda^2 - 0{\cdot}1646}\ ; \qquad \lambda_0 = 0{\cdot}4057.$$

Dextro					Laevo		
concentration g/100 c.c.	obs. [α] o	o—c	Line.	calc. [α] c	o—c	obs. [α] o	concentration g/100 c.c.
0. 3984	+843.4°	−1.1°	Cd_{5086}	±844·5°	+0·4°	−344 9°	0·4048
	745.4	+0.5	Ag_{5209}	744·9	−0·2	744·7	
	594 8	±0	Hg_{5461}	594·8	+0 6	595·4	
	468·1	−0·7	Hg_{5780}	468·8	+0·1	468·9	
	435·4	+0·4	Na_{5893}	435·0	−0·3	434·7	
	382·3	+0·3	Li_{6104}	382·0	+0·9	382·9	
	317·5	−0.5	Cd_{6438}	318 0	−0·6	317·4	
	278·6	+0·2	Li_{6708}	278·4	−0·5	277 9	

The solution did not exhibit any mutarotation.

The rotatory power determinations were made in a 2 dcm. jacketted tube at 35°. Hg_{violet}, Hg_{green}, $Hg_{yell.}$ and Na_D refer to the violet mercury line 4358, the green mercury line 5461, the yellow mercury line 5780, and the yellow sodium line 5893 respectively. In the case of 1:5-naphthylenebisaminomethylenecamphor (Table V), which shows simple rotatory dispersion, the value of λ_0 has been calculated from the dispersion formula, and is expressed as μ or 10^{-4} cm.

We wish to make grateful acknowledgment to the Government of Bihar and Orissa in the ministry of Education, for the grant of a research scholarship to one of us (B.B.) which has enabled him to take part in this investigation.

RAVENSHAW COLLEGE,
CUTTACK.

Received October 9, 1931.

The Molecular Compounds of 4:6-Dichloro-1:3 Dinitrobenzene.

By H. S. Jois and B. L. Manjunath.

Sudborough and Picton, (*J. Chem. Soc.*, 1906, **89**, 589-90), were the first to describe the molecular compounds of 4:6-dichloro-1:3-dinitrobenzene with α-and β-napthylamines. Other products of similar nature with this dichlorodinitrobenzene have now been obtained. The present paper deals with the preperation and properties of molecular compounds of the same with naphthalene, α- and β-naphthols, benzidine and pyridine. The work of Sudborough and Picton (*loc. cit.*) has also been repeated and some new interesting results have been obtained. Anthracene, dimethylaniline, diphenylamine and *o*-, *m*- and *p*-nitroanilines did not give any result.

It is interesting to note that in all cases except those of benzidine and pyridine the components are present in equimolecular ratios whereas the molecular compound with benzidine, contained two molecular proportions of dichlorodinitrobenzene and reverse was the case with pyridine which gave a dypyridonium compound.

The theories which have so far been advanced * in order to explain the structure, stability, colour and other characteristics of molecular compounds of various types, do not satisfy all cases and it is hoped that the experimental results in the present paper may throw some light upon this problem.

Experimental.

Molecular compounds of 4:6-*dichloro*-1:3-*dinitrobenzene* (A) *with naphthalene*, α-and β-*naphthols*.—Compound A was mixed with the second component in molecular proportion and melted. The fusion curve was determined according to the method of Brady and Harris (*J. Chem. Soc.*, 1923, **123**, 494), using a Pyrex test-tube and glass-rod stirrer.

* Werner, *Ber.*, 1909, **42**, 4329; Pfeiffer, *Z. anorg. Chem.*, 1920, **112**, 90; Hertel and Brömer, *Ber.*, 1930, **63**, 2446.

The molecular compounds were also prepared by mixing the components in nearly molecular proportions and crystallising the mixture from a suitable solvent. Compounds of naphthalene and α-naphthol could be obtained from benzene solution and that of β-naphthol from carbon tetrachloride. This had definite melting points and recrystallisation from the same solvents did not alter their characteristics.

Molecular compound of A with naphthalene.	Freezing point from the cooling curve.	m.p.	Colour and crystalline form.	Chlorine Found.	Chlorine Calculated.
$C_6H_2O_4N_2Cl_2$, $C_{10}H_8$ α-Napthol	68-68·1°	68°	Pale yellow prisms.	19·5	19·3 p.c.
$C_6H_2O_4N_2Cl_2$, $C_{10}H_8O$ β-Napthol	105°	105°	Orange plates.	18·5	18·6
** $C_6H_2O_4N_2Cl_2$, $C_{10}H_8$.	78·2-78·7°	78·5°	Deep yellow prisms.	18·6	18·6

Molecular compounds of A with α-and β-naphthylamines.

The molecular compound of α-naphthylamine was obtained in a pure state by mixing warm solutions of molecular proportions of the components in absolute alcohol and setting aside to cool. Dark brown prisms, m.p. 91°. (Found: Cl, 18·6. $C_6H_2O_4N_2Cl_2$, $C_{10}H_9N$, requires Cl, 18·7 per cent.).

If the above compound is dissolved in alcohol and the solution heated under reflux for some time the condensation product *2:4-dinitro-5-chlorophenyl-α-naphthylamine* gradually separates out. This substance was found to occur in two modifications, one yellow and the other orange. The former was obtained by recrystallising the crude substance from alcohol and benzene. The latter separates out sometimes from toluene. The orange compound gradually changes over into the yellow form between 145-50°. The yellow crystals melt at 204-05°. [Found (orange form): Cl, 10·1, in yellow form: 10·3; $C_{16}H_{10}O_4N_3Cl$, requires Cl, 10·3 per cent.

** This compound when dissolved in benzene or absolute alcohol readily dissociated into its components.

The compound of β-naphthylamine could be obtained in a pure state by mixing solutions of the components in warm dry benzene or better in carbon tetrachloride. Dark brown silky prisms, m.p., 72-73°. (Found: Cl, 18·6. $C_6H_2O_4N_2Cl_2$, $C_{10}H_9N$, requires Cl, 18·7 per cent.).

2:4-*Dinitro-5-chlorophenyl-β-naphthylamine* is readily formed on heating a solution of the additive compound in alcohol and is also found to exist in two forms, one orange and the other yellow. The former is obtained from a concentrated solution of the crude material in toulene and the latter from a dilute solution. In this case the yellow variety is the labile modification. The orange compound melts at 186-87°. [Found (yellow form): Cl, 10·2, in the orange isomer, 10·2; $C_{16}H_{10}O_4N_3Cl$ requires Cl, 10·3 per cent.].

The molecular compound of A with benzidine.—When equimolecular quantities of *A* and benzidine were dissolved in ether or better in carbon tetrachloride and the solutions mixed, there was rapid separation of a small quantity of dark violet crystals. These were filtered, washed and dried at 40°. The melting point could not be determined as condensation set in on warming. The compound was found to contain 21·5 per cent. of chlorine corresponding to the formula $C_{12}H_{12}N_2$, $2C_6H_2O_4N_2Cl_2$. The yield of this compound was nearly twice as much when *A* and benzidine were taken in the molecular ratio 2:1.

The Reaction of pyridine with compound A.—If pyridine (8g.) and *A* (5g.) are mixed and heated on water-bath vigorous reaction sets in with the evolution of some hydrogen chloride. The resulting brown mass was washed with ether to remove the unchanged components and extracted with cold methyl alcohol. From this extract the dipyridonium compound was precipitated out by the careful addition of ether (*d* 0·720). The process was repeated till the substance was obtained in the form of a colourless microcrystalline powder, yield, 2 g. (Found: C, 44·76; H, 3·84; N, 13·4; Cl, 16·44. $C_{18}H_{12}O_4N_4Cl_2$, $2H_2O$ requires C, 44·53; H, 3·74; N, 13·0; Cl, 16·44 per cent.).

The water of crystallisation was not removed when the substance was kept for several days in a vacuum dessicator. The compound is very soluble in water and alcohol, but insoluble in benzene and ether. It was found to be completely ionised in aqueous solution. The melting point could not be determined because on warming it gradually changed over to a yellow compound. If the aqueous

solution is heated, a yellow crystalline substance separates on cooling and the filtrate becomes acidic.

This latter (the yellow compound) was also obtained by extracting with boiling water the residue from the original reaction mixture. It is very sparingly soluble in the usual organic solvents. It did not contain any halogen and the percentage of nitrogen was found to be 16·75. It decomposed gradually at 295°. The nature of this substance is under investigation.

The halogen estimations reported in this paper were carried out with the help of Parr's bomb according to the procedure recommended by Lemp and Broderson (*J. Amer. Chem. Soc.*, 1917, **39**, 2069).

Department of Chemistry,
Central College,
Bangalore.

Received January 12, 1931.

Complexes of Zinc and Cadmium Iodides with Alkyl Sulphonium Iodides.

By Prafulla Chandra Ray, Nadiabehari Adhikari and Sanat Kumar Banerjee.

The present investigation was undertaken with the object of finding if cadmium and zinc, belonging to the same group in the periodic table and resembling in chemical behaviour mercuric mercury would yield a series of compounds, analogous to those formed by the interaction of trialkylsulphonium iodides with mercuric iodide (*J. Indian Chem. Soc.*, 1930, 7, 297).

The following compounds have been obtained by the interaction of alkyl sulphides or disulphides and alkyl iodides with cadmium and zinc iodides as enumerated below under (A) and (B) series respectively:

(A)—(1) $(Et_3S)_2\,CdI_4$. (2) $(Et_2MeS)\,CdI_3$. (3) $(Et_2PrS)_2\,CdI_4$. (4) $(Et_2BuS)\,CdI_3$.
(5) $(Me_3S)_2\,CdI_4$. (6) $(Me_2\,EtS)_2\,CdI_4$. (7) $(Me_2\,PrS)_2\,CdI_4$. (8) $(Me_2BuS)CdI_3$.
(9) $(Pr_3S)_2\,CdI_4$. (10) $(Pr_2\,EtS)\,CdI_3$. (11) $(Bu_3S)_2\,CdI_4$. (12) $(Et_3S)_2\,CdI_2\,Br_2$.

(B)—(13) $(Me_3S)_4\,ZnI_6$. (14) $(Me_2\,EtS)_2ZnI_4$. (15) $(Me_2PrS)_2ZnI_4$. (16) $(Et_3S)_2ZnI_4$.
(17) $(Et_2MeS)_2ZnI_4$. (18) $(Et_2PrS)_2ZnI_4$.

The chemical and physical properties of the above compounds have been studied and the constitutions assigned to them have been established from the following evidence.

The interaction of cadmium iodide on ethyl sulphide or diethyl disulphide and ethyl iodide leads to the corresponding product mentioned above. Thus it appears that the course of the reaction is as follows:

$$Et_2S_2 \longrightarrow Et_2S \xrightarrow{EtI} Et_3SI \xrightarrow{CdI_2} (Et_2S)_2CdI_4.$$

That diethyl disulphide loses one atom of sulphur is supported by the fact that when ammonia is added to the acetone solution of the substance, triethylsulphonium iodide separates out, CdI_2 being precipitated as $CdI_2{\cdot}2NH_3$.

The reaction of the sulphonium iodide is in fact strictly comparable to:

$$KI + CdI_2 = KCdI_3; \quad 2KI + CdI_2 = K_2CdI_4.$$

The conductivity of K_2CdI_4 and that of $(Et_3S)_2CdI_4$ have been measured in aqueous solution and the two conductivities have been found to be of the same order, suggesting that the two compounds are alike in constitution. Further evidence in support of this view of the constitution of these compounds can be gathered from the following two reactions:

$$CdI_2 + 2Et_2S + 2EtBr = 2(Et_3SBr)\cdot CdI_2 \quad \ldots (1)$$
$$CdBr_2 + 2Et_2S + 2EtI = 2(Et_3SI)\cdot CdBr_2 \quad \ldots (2)$$

The products having the melting point 150°—151° individually or when mixed, were found to be identical in both the cases. Had these been simple molecular compounds as represented in the equations above, they would have been different although isomeric. Hence the constitution would be $(Et_3S)_2\ CdBr_2I_2$ or $[CdBr_2I_2]\ldots 2Et_3S$. Several intermediate products (m p. 90°—100° and m.p. 100°—118°) isolated by the above reaction have been found to be indefinite mixtures of the above compound with cadmium iodide.

The compounds resulting from the interaction of cadmium iodide, alkyl sulphides and alkyl iodides belong mainly to the series and are analogous to K_2CdI_4 and only a few to the $KCdI_3$ series and these again are strictly comparable to the corresponding compounds in the mercury series.

The formation of compounds of the type $R\cdot CdI_3$ (R=Trialkyl sulphide group *e.g.*, Me_3S'') is probably due to their greater stability under the experimental conditions, while compounds of the type R_2CdI_4 probably result through a decomposition of the triiodide thus

$$2\,RCdI_3 = R_2CdI_4 + CdI_2.$$

The separation of CdI_2 is not an uncommon occurrence in this series of compounds. Such a view is also supported by the work of Klinger and Maassen (*Annalen*, 1889, **252**, 258), who found that cadmium sulphide, methyl iodide and methyl alcohol when heated in a sealed tube to 100° for 13—14 days, among other products give rise to a crystalline compound $CdI_2\cdot Me_3SI$, m.p. 167°—168°. When an attempt is made to recrystallise it from alcohol it loses ½ CdI_2 per molecule and is transformed into the compound $CdI_2\cdot 2\ Me_3SI$ *i.e.*,

$(Me_3S)_2CdI_4$, m.p. 185°. It is to be noted here that, with sulphides and iodides containing the alkyl radicals, compounds of the type R_2CdI_4 are always formed when they are allowed to react in any proportion whatsoever.

These complex bodies easily dissociate when dissolved in water. A comparison of the conductivity tables shows that both K_2CdI_4 and $(Et_3S)_2CdI_4$ dissociate on dilution into CdI_2 and 2KI or $2Et_3SI$, the conductivity values rising with increasing dilution. On treatment with ammonia in acetone solution, CdI_2 is precipitated as $CdI_2 2NH_3$ and the trialkyl sulphonium iodide is decomposed.

$$R_2CdI_4 + 2NH_3 = 2RI + CdI_2{\cdot}2NH_3.$$

Zinc iodide behaves like cadmium iodide so far as its action upon a mixture of alkyl iodide is concerned. The products have the general formula R_2ZnI_4 ; compounds of the formula $RZnI_3$ could not be isolated although in one instance, an anomalous result was obtained from the interaction of zinc iodide, methyl sulphide and methyl iodide, when a compound having the composition $(Me_3S)_4ZnI_6$ was isolated. The formation of this compound can be explained by assuming reactions, similar to those given for cadmium iodide compounds.

$$ZnI_2 + Me_3SI = (Me_3S\ ZnI_3\ ;\ 2(Me_3S)ZnI_3 = (Me_3S)_2ZnI_4 + ZnI_2\ ;\ 2(Me_3S)_2ZnI_4 = (Me_3S)_4ZnI_6 + ZnI_2.$$

It is not easy to ascertain why the methyl radical should have this sort of selective action. It is, however, wellknown that the first member of a series usually has anomalous properties.

The interactions between zinc iodide or cadmium iodide and (a) methyl sulphide or (b) ethyl sulphide and ethyl iodide take place violently and are exothermic. All these reactions proceed smoothly in acetone solution and are complete within half an hour.

Experimental.

(A) *Preparation of the compound* $(Et_3S)_2{\cdot}CdI_4$.—(A) Cadmium iodide, ethyl sulphide and ethyl iodide in the proportion 1 : 2 : 2 mol. (ethyl iodide in slight excess) were allowed to react in acetone solution in the cold. The reaction was complete after three hours, when crystals of the compound separated. More acetone was added to the reaction mixture to dissolve the crystalline

compound formed. Ether was added to the solution until no more white crystalline precipitate of the compound separated. The substance was recrystallised from acetone. A mixture of the three components in equimolecular proportions (alkyl iodide in excess) gave the above compound but the compound $Et_3S{\cdot}CdI_3$ was not formed at all. (B) The same compound was obtained from cadmium iodide, diethyl disulphide and ethyl iodide in the proportion 1 : 2 : 2 mol. (alkyl iodide in excess) by heating them under reflux for 1 to 2 hours without dissolving them in acetone. A tarry viscous mass separated which was dissolved in acetone. The pure compound was isolated by dissolving repeatedly in acetone and precipitating each time with ether.

Each of the compounds (white monoclinic crystals) obtained from reactions (A) and (B) melts at 156°-157°. Their mixed melting point is 156°-157°. The same compound (m.p. 145°) was also obtained by Klinger and Maassen (*loc. cit.*) by heating cadmium sulphide with ethyl iodide and ethyl alcohol at 100° for 10-15 days. (Found: Cd, 13·06; I, 58·73; C, 16·44. $(Et_3S)_2CdI_4$ requires Cd, 13·05; I, 59·2; C, 16·78 per cent.).

Analysis of the compound obtained from diethyl disulphide.—Found: Cd, 13·03; I, 58·69; C, 16·48 per cent.

Preparation of the compound K_2CdI_4.—It was prepared by the interaction of potassium iodide (2 mol.) with cadmium iodide (1 mol.) in aqueous solution. It was purified by fractional crystallisation. (Found: Cd, 15·88; I, 72·01. K_2CdI_4 requires Cd, 16·04; I, 72·78 per cent.).

Measurement of conductivity of the compounds $(Et_3S)_2CdI_4$ *and* K_2CdI_4.—The conductivity was measured by the Leeds Northrup type of Wheatstone Bridge Box at a temperature 25°.

TABLE I.

Compound from ethyl sulphide.		Compound from diethyl disulphide.		K_2CdI_4.	
Molecular concentration.	Molecular conductivity (r.o.).	Molecular concentration.	Molecular conductivity (r.o.).	Molecular concentration.	Molecular conductivity (r.o.).
·000154	443·4	·000141	463·1	·00013	524·6
·000077	482·0	·0000705	508·7	·000065	564·8
·0000385	589·4	·0000352	572·9	·0000325	595·4
·0000192	614·1	·0000176	669·9	·0000162	677·9

The conductivity data show (within experimental error) that the three compounds are of similar type. The greater difference in the case of the compound K_2CdI_4 is due to the greater mobility of the K^+ ion than that of the complex ion $(Et_3S)^+$ in $(Et_3S)_2CdI_4$, since Et_3S^+ is much heavier and more complex and sluggish in nature than the K^+ ion.

Preparation of the compound $(Et_2MeS)CdI_3$.—Cadmium iodide, ethyl sulphide, methyl iodide in the proportion 1:1:1 mol. (methyl sulphide in slight excess) were allowed to react in acetone solution in the cold for two days after which the mixture was diluted with acetone and the compound was precipitated by adding ether. The precipitated compound was purified by repeatedly dissolving in acetone and precipitating by ether. It was finally crystallised from acetone.

The same compound was obtained from equimolecular proportion of the components.

Properties.—It is a white crystalline solid, m.p. 75°, highly soluble in acetone and also in methyl alcohol. It is isomorphous with the other members of the series. (Found: Cd, 18·69; I, 63·66; C, 9·85. $(Et_2MeS)CdI_3$ requires, Cd, 18·73; I, 63·71; C, 10·03 per cent.).

Preparation of the compound $(Et_2PrS)_2CdI_4$.—The components cadmium iodide, ethyl sulphide, *n*-propyl iodide in the proportion 1:2:2 mol. with the alkyl iodide in slight excess were mixed in acetone solution in the cold. The mixture was shaken at intervals and was allowed to remain for five days, when the reaction was found to be nearly complete. The compound was isolated in the usual manner by repeating the process of dissolving in acetone and precipitation with ether. The precipitated compound was crystallised from acetone.

From equimolecular mixture of the three components, the same compound was obtained; not even a trace of $(Et_2PrS)CdI_3$ could be isolated.

Properties.—It is a crystalline monoclinic solid, m.p. 150°, very soluble in acetone, but less so than the methyl iodide compound of this series. (Found: Cd, 12·68; I, 57·05. $(Et_2PrS)_2CdI_4$ requires Cd, 12·64; I, 57·84 per cent.).

Preparation of the compound $(Et_2BuS)CdI_3$.—It was prepared in the same manner as the propyl iodide compound of this series, the components being cadmium iodide, ethyl sulphide and *n*-butyl iodide. The compound isolated from the two sets of reactions was

identical and not even a small amount of $(Et_2BuS)_2CdI_4$ was obtained.

Properties.—The compound (m.p. 116°) is highly soluble in acetone and is the most soluble compound of this series. The crystals are isomorphous with the other members of the series. (Found: Cd, 17·46; I, 59·57 per cent. $(Et_2BuS)CdI_3$ requires Cd, 17·5; I, 59·53 per cent.).

Preparation of the compound $(Et_3S)_2{\cdot}CdI_2Br_2$.—Cadmium iodide, ethyl sulphide, ethyl bromide in the proportion 1:2:2 mol. were mixed together in acetone solution in the cold (with the alkyl bromide in excess). The mixture was allowed to remain at the ordinary temperature for two days and was shaken at intervals. The mixture was then diluted with acetone and was treated with ether until the precipitation was complete. The precipitate was again dissolved in acetone and reprecipitated in the crystalline state by ether.

The white crystalline precipitate thus obtained was recrystallised from acetone. The first crop of the crystals which separated within an hour melted at 145°-150°. It was then washed with a little acetone, redissolved in acetone and the first fraction that was obtained this time after an hour was found to melt sharply at 150°-151°. A proportion of it was also crystallised from methyl alcohol and the crystals so obtained were found to melt sharply at 150°-151°, thus confirming the purity of the substance.

After the separation of the first fraction, two crops of crystals were also obtained from the mother liquor, but each of these fractions was found to melt within a wide range of temperature, the second crop melting between 110°-120° and the third between 95°-105°.

In precisely similar manner and under similar conditions, by taking the components cadmium bromide, ethyl sulphide and ethyl iodide, similar crops of crystals were isolated. The first one was obtained in quantity and it was purified as described in the other reaction and was found to melt at 150°-151°.

Thus the compound isolated from the interaction of cadmium bromide, ethyl sulphide and ethyl iodide was identical with that obtained from the same sulphide and ethyl bromide and cadmium iodide, each having the melting point 150°-151° and the mixed melting point was also 150°.

Properties.—It is a white crystalline solid. The crystals have monoclinic form. It is sparingly soluble in acetone in the cold.

Analysis of the compound obtained from cadmium iodide, ethyl sulphide and ethyl bromide.—Found: Cd, 14·86; Br+I, 54·31; C, 18·52 per cent.

Analysis of the compound obtained from cadmium bromide, ethyl sulphide and ethyl iodide.—Found: Cd, 14·88; Br+I, 54·34 per cent.

$(Et_3S)_2CdBr_2I_2$ requires Cd, 14·53 ; Br+I, 54·18 ; C, 18·14 per cent.

TABLE II.

Conductivity in aqueous solution.

Temp. = 30°.

Mol concentration	... ·001093	·0005165	·0002582	·0001291	·0000645
Mol conductivity (r.o.)	... 397·4	431 4	457 4	494 4	548·3

From a comparison of the above table with Table I, it would appear that this compound is of the same type as those in Table I.

Preparation of the compound $(Me_3S)_2CdI_4$.—Acetone solutions of cadmium iodide (1 mol.) and methyl sulphide (2 mol.) (a) were mixed together in the cold. To the mixture was added an excess of methyl iodide about (1 mol.). Gradually crystals of the compound began to separate. The reaction was complete in an hour. The compound was isolated in the usual manner and crystallised from methyl alcohol.

In whatever proportion the components were allowed to react, the compound $(Me_3S)_2CdI_4$ was always formed. But the yield was maximum when they were mixed together in the proportion mentioned above.

(b) The same compound can be obtained from dimethyl disulphide, methyl iodide and cadmium iodide by heating the components at the temperature of water-bath for 5-6 hours. In this case and also with diethyl disulphide, the reaction did not take place at the ordinary temperature nor did the components react when their acetone solution was kept for days together.

The crystals obtained from both reactions (a) and (b)from methyl alcohol or acetone solution melted at 204°, which was also the melting point of the compound obtained from dimethyl disulphide. The mixed melting point was 203°-204°.

Properties.—It is a white crystalline (monoclinic) substance. It is sparingly soluble in acetone or methyl alcohol and also in boiling water, though a certain amount of the substance decomposes in this solvent.

The same compound was isolated by Klinger and Maassen (*loc. cit.*) by heating cadmium sulphide with methyl iodide and methyl alcohol for 13-14 days in a sealed tube at 100°. (Found: Cd, 14·44; I, 65·27; C, 9·3. $(Et_3S)_2\ CdI_4$ requires Cd, 14·47; I, 65·63; C, 9·3 per cent.).

Analysis of the compound obtained from dimethyldisulphide.—Found: Cd, 14·46; I, 65·24; C, 9·27 per cent.

Preparation of the compound $(Me_2EtS)_2\ CdI_4$.—Dimethyl sulphide, ethyl iodide and cadmium iodide were allowed to react in acetone solution at the ordinary temperature.

Properties.—It is a white crystalline (menoclinic) solid, m. p. 185.° It is more soluble in methyl alcohol or acetone than the compound mentioned above. (Found: Cd, 13·94; I. 63·11. $(Me_2EtS)_2CdI_4$ requires Cd, 13·97; I, 63·34 per cent.).

Preparation of the compound $(Me_2PrS)_2CdI_4$.—This compound was prepared (a) in the same way as the previous one using *n*-propyl-iodide in place of ethyl iodide but in this case the reaction took 4 days to complete ; and (b) by heating the components on the water-bath under reflux but with diminished yield.

Properties.—It is a white monoclinic crystalline solid, very soluble in either methyl alcohol or acetone, warm or cold, from which it crystallises slowly, m.p. 120°. (Found: Cd, 13·52; I, 60·74; C, 14·23 . $(Me_2PrS)_2CdI_4$ requires Cd, 13·49; I, 61·2; C, 14·46 per cent.).

Preparation of the compound $(Me_2BuS)\ CdI_3$.—This compound (white monoclinic crystals, m.p. 130°) was prepared by the general method at laboratory temperature in acetone solution, the duration of the reaction being four days.

When the components were heated together under reflux on the water-bath for four to five hours without dissolving them in acetone, a tarry mass was obtained. By the usual process of extraction, a crystalline precipitate was obtained (from the tarry mass). The compound was recrystallised from methyl alcohol, m.p. 203°-204°. The yield was extremely small. The compound thus isolated was found to be identical with $(Me_3S)_2CdI_4$ and like the latter it was also found to be sparingly soluble in acetone.

It may be that during the process of heating, dimethylbutylsulphonium iodide was formed and decomposed into methylbutylsulphide, giving rise to trimethylsulphonium iodide which, in turn, combined with cadmium iodide, yielding the compound $(Me_3S)_2CdI_4$.

The behaviour of the sulphonium iodide has also been studied by Smiles (*J. Chem. Soc.*, 1900, 77, 160), Klinger and Maassen (*loc. cit.*). (Found: Cd, 18·23; I, 62·22; C, 18·54. (Me_2BuS) CdI_3 requires Cd, 18·3; I, 62·25; C, 11·76 per cent.).

Preparation of the compound $(Pr_3S)_2CdI_4$.—To the acetone solution of cadmium iodide (1 mol.) were added *n*-propyl sulphide (2 mol.) and *n*-propyl iodide (2 mol.) and the mixture was kept at the ordinary temperature for a day (the alkyl iodide was added in slight excess). The compound was isolated in the usual manner by the use of acetone and ether. It was finally recrystallised from acetone. When the reaction was started with equimolecular mixture of the components, the same compound was also isolated at the end.

Properties.—The compound (white crystals, m.p. 151°-152°) is highly soluble in acetone, even in the cold and is in fact more soluble than the other two compounds of the series having the same alkyl radicals in the sulphonium iodide group. (Found: Cd, 11·85; I, 53·99. $(Pr_3S)_2CdI_4$ requires Cd, 11·89; I, 53·93 per cent.).

Preparation of the compound (Pr_2EtS) CdI_3.—The preparation was started with cadmium iodide, *n*-propyl sulphide and ethyl iodide in equimolecular proportion and also in another operation in the proportion 1 : 2 : 2 mol., the alkyl iodide being added in excess (about 2-3 g.). The reaction was allowed to take place in acetone solution in the cold for three days. The compounds that were isolated from each operation by the use of acetone and ether in the usual manner were found to be identical and to have the same melting point.

Properties.—It is a white crystalline solid, highly soluble in acetone, m.p. 77°-78°. (Found: Cd, 17·38; I, 59·26; C, 14·76. (Pr_2EtS) CdI_3 requires Cd, 17·50; I, 59·53; C, 15·0 per cent.).

Preparation of the compound $(Bu_3S)_2CdI_4$.—Cadmium iodide, butyl sulphide and butyl iodide in the proportion 1 : 2 : 2 mol. (butyl iodide in excess) were mixed up together in acetone solution and the components were allowed to react for two days. The compound was isolated in the usual manner by the use of acetone and ether.

Properties.—The compound (monoclinic crystalline solid m. p. 110°) is highly soluble in acetone. In fact, it is the most soluble of

all the compounds of the series having the same alkyl radicals in the sulphonium iodide group. (Found: Cd, 11·15; I, 50·05. $(Bu_3S)_2$ CdI_4 requires Cd, 10·92; I, 49·51 per cent.).

Preparation of the compound CdI_2, $2NH_3$—To the acetone solution of $(Et_3S)_2CdI_4$, ammonia was passed until no more white precipitate was formed. The precipitate was filtered, and then washed several times with acetone to free it from any undecomposed substance. The filtrate was warmed a little to remove ammonia and then on cooling, it was treated with ether, when a yellow precipitate separated out. The yellow precipitate was crystallised from acetone. The yellowish crystalline substance (m. p. 145°-148°) was found to be identical with the triethyl sulphoniumiodide, prepared by the interaction of ethyl sulphide and ethyl iodide. The triethyl sulphonium iodide being very hygroscopic, the melting point was not so sharp. In precisely similar manner, triethyl sulphoniumiodide was isolated from the compound obtained from cadmium iodide, diethyl disulphide and ethyl iodide, proving thereby the fact that one sulphur atom of ethyl disulphide was lost during its interaction with cadmium iodide and ethyl iodide. The white precipitate that was formed by passing ammonia was found to be CdI_2, $2NH_3$. (Found: Cd, 28·2; I, 68·50. CdI_2, $2NH_3$ requires Cd, 27·98; I, 68·75 per cent.).

Preparation of the compound $Me_3S_4 \cdot ZnI_6$.—Zinc iodide, methyl sulphide and methyl iodide in the proportion 1:2:2 mol. were allowed to react in acetone solution in the cold (methyl iodide being added in slight excess). The reaction was complete within half an hour, after which it was diluted with a little acetone and treated with ether. A white crystalline precipitate separated out. The precipitate was washed with a little acetone in order to free it from any unreacted zinc iodide and it was then recrystallised from acetone. The reaction was also started with the components in equimolecular proportion, but at the end, the one and same compound was obtained, not even a trace of $(Me_3S)ZnI_3$ or $(Me_3S)_2ZnI_4$ being formed. The same compound was also obtained by the use of dimethyl disulphide instead of using methyl sulphide in the above reaction. But in this case, the reaction mixture was heated on the water-bath for one hour without dissolving the components in acetone. At the ordinary temperature, however, no reaction took place.

Properties.—It is a lustrous white crystalline (rhombic) solid. It is sparingly soluble in acetone or methyl alcohol. Each of the

compounds obtained from methyl sulphide and methyl disulphide melts at 208°. Their mixed melting point is 207°-208°. (Found: Zn, 5·77; I, 66·99; C, 12·39. $(Me_3S)_4ZnI_6$ requires Zn, 5·73; I, 67·1; C, 12·69 per cent.).

Preparation of the compound $(Me_2EtS)_2ZnI_4$.—It was obtained from the action of zinc iodide in acetone solution in the cold, upon methyl sulphide and ethyl iodide. The components were taken in the proportion 1:2:2 mol. (the alkyl iodide was added in excess). The reaction was complete after four hours. The compound was isolated in the usual manner by using acetone and ether. It was recrystallised from acetone. By varying the proportion of the reactants the same compound was always obtained.

Properties.—It is a white crystalline substance, m.p. 184°-185°. It is more soluble in acetone or methyl alcohol than the triethyl sulphonium compound mentioned above. (Found: Zn, 8·51; I, 67·36; C, 12·43. $(Me_2EtS)_2ZnI_4$ requires Zn, 8·61; I, 67·28; C, 12·72 per cent.).

Preparation of the compound $(Me_2PrS)_2ZnI_4$.—Zinc iodide, methyl sulphide and propyl iodide were allowed to react in acetone solution in the proportion 1:2:2 mol. for four days at the ordinary temperature, when the reaction was found to be complete. The compound was isolated in similar manner as mentioned above. It melts at 132°-133°. (Found: Zn, 8·28; I, 64·74; C, 15·09. $(Me_2PrS)_2ZnI_4$ requires Zn, 8·3; I, 64·88; C, 15·33 per cent.).

Preparation of the compound $(Et_3S)_2ZnI_4$.—The components, zinc iodide, ethyl sulphide and ethyl iodide in the proportion 1:2:2 mol. (the alkyl iodide was aded in slight excess) were allowed to react in acetone solution at the ordinary temperature for two hours when the reaction was found to be complete. The compound was isolated from the reaction mixture by the use of acetone and ether. It was finally recrystallised from acetone. The same compound was also obtained by using ethyl disulphide instead of ethyl sulphide in the above reaction. But in this case the components were heated under reflux on the water-bath.

The compound obtained from either ethyl sulphide or ethyl disulphide melts at 149° and their mixed melting point is 148°-149°. (Found: Zn, 8·12; I, 62·52; C, 17·43. $(Et_3S)_2ZnI_4$ requiresZn, 8·01; I, 62·64; C, 17·75 per cent.).

TABLE III.

Conductivity in aqueous solution.

Temp. = 30.

Mol. concentration	...	·00478	·002865	·0011825	·0005912	·0002956
Mol. conductivity (r. o.)	...	438·5	4790	492·6	506·9	519·6

It will be evident from a comparison of Table III with Tables I and II that this compound is also of similar type to the compound in the other tables.

Preparation of the compound $(Et_2MeS)_2ZnI_4$.—In this preparation too, the components zinc iodide, ethyl sulphide, methyl iodide were allowed to react in acetone solution in the proportion 1:2:2 mol. (methyl iodide being added in slight excess). The reaction was complete after three days. The product was isolated and purified in the same way as other compounds of the series. It was recrystallised from acetone. Not even a trace of the compound of the type $KZnI_3$ was obtained by carrying out the reaction with equimolecular proportion of the components.

Properties.—It is a white crystalline solid, m.p. 173°-174°, highly soluble in acetone, methyl alcohol, water, etc. The crystals are isomorphous with the other members of the series. (Found: Zn, 8·21; I, 64·22; C, 15·11. $(Et_2MeS)_2$ ZnI_4 requires Zn, 8·32; I, 64·88; C, 15·33 per cent.).

Preparation of the compound $(Et_2PrS)_2ZnI_4$.—It was prepared by the interaction of zinc iodide with ethyl sulphide in the proportion 1:2:2 mol. (the alkyl iodide was added in slight excess) in acetone solution and isolated in a like manner.

Properties.—It is a white crystalline (monoclinic) solid m.p. 145°. It is soluble in acetone, methyl alcohol, water, etc., and is in fact the most soluble compound of the series. (Found: Zn, 7·62; I, 60·12; C, 19·65. $(Et_2PrS)_2$ ZnI_4 requires Zn, 7·74; I, 60·55; C, 20·02 per cent.). In all the reactions cited above, about 50-60% yield of the compound was obtained.

Preparation of zinc ammonia compound and isolation of the triethyl sulphonium iodide.—Through the acetone solution of $(Et_3S)_2$ ZnI_4, ammonia was passed until the precipitation of the white zinc ammonia compound was complete. The precipitate was several times washed with acetone. It was thus purified and then dried

from the filtrate; triethyl sulphonium iodide was isolated by the precipitation of the latter with ether, as in the case of the analagous cadmium iodide compound. (Found: Zn, 16·54; I, 65·94. ZnI_2, $4NH_3$ requires Zn, 17·79; I, 66·68 per cent.).

PALIT PROFESSOR'S LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
CALCUTTA.

Received July 14, 1931.

On the Mechanism of Unimolecular Reactions.

By A. Ganguli.

The radiation theory of chemical reactions gives the number of activated molecules as follows:

$$N_a = N\int_{\nu_0}^{\infty} e^{-\frac{h\nu}{kT}}\,d\nu,$$

where N is the number of normal molecules and ν_0 is the threshold frequency. Thus the velocity coefficient assumes the form

$$k_1 = \frac{1}{N}\cdot\frac{dN}{dt} = \frac{N_a}{N} = \frac{kT}{h}\cdot e^{-\frac{h\nu_0}{kT}} \quad \ldots \quad (1).$$

Equation (1) resembles an equation due to Herzfeld (*Ann. phys.*, 1919, **57**, 635). A continuous absorption band in the infra-red of the reactant should begin from this region, which is however not always the case. Moreover, all unimolecular reaction velocities are highly accelerated by external conditions, as they should be according to the above. Lindemann's collisional theory (*Trans. Farady Soc.*, 1922, **17**, 598) has also been shown to be inadequate (Christiansen aud Kramers, *Z. Phys. Chem.*, 1923, **104**, 451). Further, the mechanism of the initial activation and parting off with the energy in the chain of reactions assumed by the 'chain theory' is not clear. In the present paper, the problem is dealt with in a different fashion.

In a previous paper (*Phil. Mag.*, 1931, *vii*, **12**, 583 ; see also, *Z. Physik.*, 1930, **61**, 411), two expressions for the velocity for unimolecular reactions have been deduced from the following considerations. In both cases, it is assumed that the normal molecules are activated by the absorption of infra-red radiation, and these activated molecules subsequently decompose, either in a manner similar to that involved in thermionic emissions, or by a process of

desorption. According to the first hypothesis, a statistical equilibrium between the 'free' active molecules and 'bound' active molecules is considered, and finally the following expression is obtained (*Phil. Mag., loc. cit.*) :

$$k_1=\frac{2\pi\,\mu\,k^2}{h^3}.T.\frac{\beta_0}{B}.\,e^{-\frac{Q_{AB}}{RT}}, \qquad \ldots \quad (2)$$

where μ, the effective mass, equals $\frac{1}{m_A}+\frac{1}{m_B}$, m_A and m_B being the masses of the resultants; β_v is the effective collisional area of recombination and $\beta_0=T.\beta_v$, B (or 'a') is the statistical weight factor. It may be noted that the critical increment Q_{AB} is composed of two factors, the radiant energy and the heat of dissociation Q_0 (corresponding to the ionisation potential in thermionic emission) and may also be expressed as $N.h.\nu_{AB}$, ν_{AB} is a virtual frequency, given as the sum of ν_0 and $\nu_a\left(=\frac{Q}{Nh}\right)$. This expression is similar to that obtained by Roy (*Proc. Roy. Soc.*, 1926, **A**,**110**, 548) but differs by the factor 4, though derived from different considerations. Roy suggests a mechanism of photo-electric effect, and thereby claims the validity of the radiation hypothesis. It is possible that isolated instances exist where $Q=0$, and the reaction velocity depends solely on the infra-red frequency, in cases equation (1) may be valid and absorption band in the region of ν_0 should be obtained, as was found by Lewis in the case of inversion of sucrose By introducing the values of the universal constants and taking logarithms of the expressions in equation (2), we have

$$\log_{10} k_1=\log_{10} T+\log_{10} S-\frac{b}{T}, \qquad \ldots \quad (3)$$

where $b=\frac{Q}{2{\cdot}3\,R}$ and $S=\frac{2\pi\,\mu\,k^2}{h^3}.\frac{\beta}{a}$; b is calculated from the values of k_1, at two temperatures. Substituting the average value of b and the corresponding value of k_1 and T in the above equation,

we obtain S. Again from the value of μ and S, we get the values of $\frac{\beta_0}{a}$ for different reactions. The values of $k_{1\text{cal.}}$ and $k_{1\text{obs.}}$ and also of $\frac{\beta_0}{a}$ for different reactions are given in the following tables.

The real significance β_0 and a is not clear. Roy (*loc. cit.*) attributes to β_0 the value of the area of a circle, whose radius is the sum of the radii of the resultant products. This can be understood from the recent work of London (*Z. Physik.*, 1930, **63**, 245). If we assume this distance to depend on the pressure of the system at very low pressure, then the reaction velocity will be affected by the pressure under those circumstances, as has been experimentally observed by several authors (Rice and Ramsperger, *J. Amer. Chem. Soc.*, 1927, **49**, 1617; Ramsperger, *ibid.*, 1917. **49**, 1495). The statistical factor, a may be taken to be twice the number of bonds, as suggested by Roy.

TABLE I.

Decomposition of diethyl ether.

[Hinshelwood, *Proc. Roy Soc.*, 1927, **A**,**114**, 84].

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O \longrightarrow [C_2H_6 + C_2H_4O]$$
$$\longrightarrow C_2H_4 + CO + CH_4.$$

$$\log_{10}k_1 = 8{\cdot}7578 + \log_{10}T - \frac{11512}{T}.$$

T	$k_{\text{obs.}}$	$k_{\text{cal.}}$
861	·0103	·0103
828·5	·00262	·00597
798	·000851	·0001697
49	·0000861	·00002447
699	·000000736	·000001356

$Q = 52480$ cal.
$\beta_0/a = 4{\cdot}671 \times 10^{-17}$
(for the resultants $C_2H_6 + C_2H_4O$)
or $\beta_0/a = 1{\cdot}069 \times 10^{-16}$
(for the resultants $C_2H_6 + CO + CH_4$).

TABLE II.

Decomposition of dimethyl ether.

[Hinshelwood and Askey, *Proc. Roy. Soc.*, 1927, **A**,**115**, 215].

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!O \longrightarrow [CH_4 + COH_2]$$
$$= CH_4 + CO + H_2.$$

$$\log_{10}k_1 = 9{\cdot}2980 + \log_{10}T - \frac{12103}{T}.$$

T	$k_{\text{obs.}}$	$k_{\text{cal.}}$
825	·00431	·00431
795	·00113	·00117
777	·000544	·000511
751	·000127	·0001391
725	·0000317	·0000362
695	·00000147	·000006459

$Q = 55170$ cal.
$\beta_0/a = 8\ 414 \times 10^{-16}$ (for the resultants $CH_4 + CO + H_2$)
or $\beta_0/a = 1\ 687 \times 10^{-15}$ (for the resultants $CH_4 + CO + H_2$).

TABLE III.

Decomposition of acetone. [Hinshelwood and Hutchison, *Proc. Roy. Soc.*, 1926, **A**, **111**, 245].

$$CH_3 \cdot CO \cdot CH_3 \longrightarrow C_2H_6 + CO.$$

$$\log_{10} k_1 = 10{\cdot}795 + \log_{10} T - \frac{13791}{T}.$$

T	$k_{obs.}$	$k_{cal.}$
904·5	·03677	·03172
890	·01670	·01756
857	·004946	·004846
809	·000462	·0004102
790	·0001557	·0001559
779	·00007254	·00008843

$Q = 57860$ cal.

$\beta_0/a = 6{\cdot}275 \times 10^{-15}$.

TABLE IV.

Decomposition of ethylene oxide. [Winfield, Heckert and Mack, *J. Amer. Chem. Soc.*, 1929, **51**, 2706].

$$\begin{matrix} CH_2 \\ CH_2 \end{matrix} \!\!> \longrightarrow CO + CH_2.$$

$$\log_{10} k_1 = 11{\cdot}547 + \log_{10} T - \frac{11184}{T}.$$

T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
717·8	7·93	8·00
707·0	4·58	4·585
697·0	2·49	2·582
687·0	1·54	1·564
672·1	0·622	0·637
651·5	0·191	0·191

$Q = 53720$ cal.

$\beta_0/a = 7{\cdot}868 \times 10^{-15}$.

TABLE V.

Decomposition of $CH_3N_2C_3H_7$. [*Ramsperger, J. Amer. Chem. Soc.*, 1929, **51**, 2134].

$$C_3H_7N_2CH_3 \longrightarrow C_4H_{10} + N_2.$$

$$\log_{10} k_1 = 13{\cdot}497 + \log_{10} T - \frac{10821}{T}.$$

T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
533	0·09414	0·0544
543	0·1958	0·220
568	0·7142	0·714
573	2·372	1·69
595	11·80	6·9
605	25·05	9·8

$Q = 45140$ cal.
(Q varies widely with temperature).

$\frac{\beta_0}{a} = 2{\cdot}425 \times 10^{-13}$.

TABLE VI.

Decomposition of diazobenzene chloride. [Cain and Nicoll, *J. Chem. Soc.*, 1903, **83**, 470].

$$C_6H_5N_2Cl,\ H_2O \longrightarrow C_6H_5OH + N_2 + HCl.$$

$$\log_{10} k_1 = 11{\cdot}475 + \log_{10} T - \frac{5008}{T}.$$

T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
298	0·72	0·7101
303	2·95	2·669
313	8·87	9·133
323	29·8	29·81
333	109·3	90·63

$Q = 22830$ cal.

$\frac{\beta_0}{a} = 8{\cdot}221 \times 10^{-14}$.

TABLE VII.

Decomposition of diazotoluide chlorides. [Cain and Nicoll, *J. Chem. Soc., loc. cit.*]. $CH_3C_6H_4N_2Cl,H_2O \rightarrow CH_3{\cdot}C_6H_4OH + HCl$.

	ortho.		*para.*		*meta.*	
	$\log_{10}k_1 = 13{\cdot}2049 + \log_{10}T - \frac{5393}{T}$.		$\log_{10}k_1 = 12{\cdot}2995 + \log_{10}T - \frac{5519}{T}$.		$\log_{10}k_1 = 11{\cdot}6623 + \log_{10}T - \frac{4924}{T}$.	
T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
293	1·87	1·869	—	—	2·085	2·084
303	7·06	7·879	0·289	0·289	6·96	7·65
313	23·80	30·23	0·999	1·134	25·7	26·78
323	102·70	43·05	3·58	4·157	—	—
333	—	—	12·0	13·87	—	—
343	—	—	46·1	44·14	—	—
	$Q = 24360$ cal.		$Q = 25447$ cal.		$Q = 23650$ cal.	
	$\frac{\beta_0}{\alpha} = 1{\cdot}687 \times 10^{-15}$.		$\frac{\beta_0}{\alpha} = 1{\cdot}666 \times 10^{-13}$.		$\frac{\beta_0}{\alpha} = 4{\cdot}837 \times 10^{-14}$.	

TABLE VIII.

Decomposition of trichloroacetic acid. [Goldschmidt and Bauer, *Ber.*, 1906, **41**, 109].

$CCl_3COOH \longrightarrow CHCl_3 + CO_2$.

$\log_{10} k_1 = 15{\cdot}4875 + \log_{10}T - 6123/T$.

T	$k_{obs.}$	$k_{cal.}$
298	0·0023	0·0023
318	0·046	0·0561

$\frac{\beta_0}{\alpha} = 1{\cdot}780 \times 10^{-10}$.

TABLE IX.

Decomposition of camphoric acid. [Bredig and Balcom, *Ber.*, 1906, **41**, 740].

$C_{10}H_{15}O\,COOH \longrightarrow C_{10}H_{16}O + CO_2$.

$\log_{10}k_1 = 11{\cdot}8851 + \log_{10}T - \frac{6854}{T}$. $\log_{10}k_1 = 11{\cdot}6586 + \log_{10}\,T - \frac{6048}{T}$.

T	$k_{obs.} \times 10^3$ (water).	$k_{cal.} \times 10^3$.	$k_{obs.} \times 10^3$ (benzene).	$k_{cal.} \times 10^3$.
34	—	—	0·306	0·289
351	0·214	0·214	0·955	0·9414
361	0·681	0·000	2·89	2·924
371	2·18	2·11	8·47	8·47
	$Q = 30330$ cal.		$Q = 27570$ cal.	
	$\frac{\beta_0}{\alpha} = 2{\cdot}606 \times 10^{-14}$.		$\frac{\beta_0}{\alpha} = 1{\cdot}544 \times 10^{-14}$.	

TABLE X.

Decomposition of nitrous oxide at different pressures. [Nagasako and Volmer, *Z Phys. Chem.*, 1930, **B,10**, 414; *cf.* Hinshelwood, *ibid.*, 1930, **B,10**, 157].

$$N_2O \longrightarrow N_2 + O.$$

$\log_{10}k_1 = 7{\cdot}5374 + \log_{10}T - \frac{11183}{T}$. $\log_{10}k_1 = 7{\cdot}3501 + \log_{10}T - \frac{10666}{T}$.

	Pressure = 1000 mm.		Pressure = 8000 mm.	
T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
938	4·3	3·887	9·6	9·6
925	3·2	2·591	2·4	2·996
898	1·0	0·9517	1·6	1·358
877	0·62	0·620	0·48	0·4995

TABLE XI.

Decomposition of propionic aldehyde. [Hinshelwood and Thomson, *Proc. Roy. Soc.*, 1927, **A,113**, 221].

$$CH_3{\cdot}CH_2{\cdot}CHO \longrightarrow C_2H_6 + CO.$$

$\log_{10}k_1 = 9{\cdot}2075 + \log_{10}T - \frac{11810}{T}$.

T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
877	39·4	49·03
849	15·6	17·24
822	5·67	5·92
796	1·85	1·898
765	0·45	0·458
722	0·052	0·052

$Q = 5500$ cal. $\beta_0/a = 1{\cdot}622 \times 10^{-16}$.

TABLE XII.

Decomposition of azomethane. [Ramspsperger, *J. Amer. Chem. Soc.*, 1927, **49**, 912].

$$CH_3N_2CH_3 \longrightarrow C_2H_6 + N_2.$$

$\log_{10}k_1 = 12{\cdot}9896 + \log_{10}T - \frac{11085}{T}$.

T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
551·6	·05	·0448
560·8	·10	·095
571·2	·252	·227
578·3	457	·400
586·7	·747	·755
600·4	2·08	2·08

$Q = 50510$ cal. $\beta_0/a = 1{\cdot}027 \times 10^{-13}$.

TABLE XIII.

Decomposition of nitryl chloride. [Schumacher and Sprenger, *Z. Phys. Chem.*, 1931, **B**,12, 123].

$$NO_2Cl \longrightarrow NO_2 + Cl.$$

$$\log_{10} k_1 = 10{\cdot}796 + \log_{10} T - \frac{5957}{T}.$$

T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
373	2·63	2·948
403	34·8	34·8
413	82·2	80·0
423	95·2	174·8

$Q = 274000$ cal. $\beta_0/\alpha = 4{\cdot}551 \times {}^{-15}$.

TABLE XIV.

Decomposition of azoisopropane. [Ramsperger, *J. Amer. Chem. Soc.*, 1928, **50**, 714].

$$C_3H_7N_2C_3H_7 \longrightarrow C_3H_{14} + N_2.$$

$$\log_{10} k_1 = 11{\cdot}0171 - \log_{10} T - \frac{8926}{T}.$$

T	$k_{obs.} \times 10^3$.	$k_{cal.} \times 10^3$.
523	0·461	0·461
533	1·03	0·986
543	2·01	2·05
553	3·88	4·167
563	7·96	8 033

$Q = 406000$ cal. $\beta_0/\alpha = 7{\cdot}196 \times 10^{-15}$.

TABLE XV.

Racemisation of pinene.

$$C_{10}H_{16} \longrightarrow C_{10}H_{16}.$$

[Smith, *J. Amer. Chem. Soc.*, 1927, **49**, 43].

$$\log_{10} k_1 = 12{\cdot}9219 + \log_{10} T - \frac{9262}{T}.$$

T	$k_{obs.} \times 10^5$.	$k_{cal.} \times 10^5$.
457°	2·20	2·20
471·0	8·57	8·412
490·9	58·0	55·33
503·9	169·0	175·6
510·4	307·0	389·0

$Q = 42220$ cal. $\beta_0/\alpha = 8{\cdot}956 \times 10^{-14}$.

TABLE XVI.

Reaction.	β_0/α.	No. of bonds.	α.	β_0.
$CH_3\rangle O \rangle CH_3 \longrightarrow CH_4 + COH_2$	$3{\cdot}414 \times 10^{-16}$	HOH=	4	$1{\cdot}36 \times 10^{-15}$
$CH_3\rangle O \rangle CH_3 \longrightarrow CH_4 + CO + H_2$	$1{\cdot}687 \times 10^{-15}$	≡CO—	8	$1{\cdot}5 \times 10^{-14}$
$C_2H_5\rangle O \rangle C_2H_5 \longrightarrow C_2H_6 + C_2H_4O$	$4{\cdot}671 \times 10^{-17}$	$CH_3{\cdot}CHO$=	4	$1{\cdot}8 \times 10^{-16}$
$\longrightarrow C_2H_6 + CO + CH_4$	$1{\cdot}069 \times 10^{-16}$	≡CO—	8	$8{\cdot}55 \times 10^{-14}$
$CH_3\rangle CO \rangle CH_3 \longrightarrow C_2H_6 + CO$	$6{\cdot}273 \times 10^{-15}$	≡CO—	8	$4{\cdot}9 \times 10^{-14}$
$CH_2\rangle O \rangle CH_2 \longrightarrow CH_4 + CO$	$7{\cdot}869 \times 10^{-14}$	≡CO—	8	$6{\cdot}2 \times 10^{-13}$
$C_3H_7\rangle N_2 \rangle CH_3 \longrightarrow C_4H_{10} + N_2$	$2{\cdot}425 \times 10^{-13}$	—N : N—	4	$9{\cdot}7 \times 10^{-13}$
$C_3H_7\rangle N_2 \rangle C_3H_7 \longrightarrow C_6H_{14} + N_2$	$7{\cdot}196 \times 10^{-15}$	,,	4	$2{\cdot}8 \times 10^{-14}$
$CH_3\rangle N_2 \rangle CH_3 \longrightarrow C_2H_6 + N_2$	$1{\cdot}027 \times 10^{-12}$	,,	4	$4{\cdot}1 \times 10^{-12}$
$C_6H_5\rangle N_2 \rangle H_2O{\cdot}Cl \longrightarrow C_6H_5OH + N_2 + HCl$	$3{\cdot}221 \times 10^{-14}$	,,	4	$1{\cdot}28 \times 10^{-13}$
(o) $CH_3{\cdot}C_6H_4\rangle N_2 \rangle H_2O{\cdot}Cl \longrightarrow CH_3C_6H_4OH + N_2 + HCl$	$1{\cdot}687 \times 10^{-12}$	,,	,,	$6{\cdot}7 \times 10^{-12}$
(p) ,, ,, ,,	$1{\cdot}666 \times 10^{-13}$	,,	,,	$6{\cdot}6 \times 10^{-13}$
(m) ,, ,, ,,	$4{\cdot}837 \times 10^{-14}$	,,	,,	$1{\cdot}98 \times 10^{-13}$
$N_2O_5 \longrightarrow N_2O_4 + O$	$7{\cdot}36 \times 10^{-15}$	=O	4	$2{\cdot}9 \times 10^{-14}$
$PH_3 \longrightarrow P + 3H$	$16{\cdot}0 \times 10^{-15}$	≡P	6	$6{\cdot}4 \times 10^{-14}$
$NO_2Cl \longrightarrow NO_2 + Cl$	$4{\cdot}551 \times 10^{-15}$	Cl=	4	$9{\cdot}1 \times 10^{-15}$
$COOEt\rangle CO{\cdot}CHOEt \rangle COOEt \longrightarrow CO + COOEt\rangle CHOEt \rangle COOEt$	$5{\cdot}4 \times 10^{-14}$	≡C—O—	8	$4{\cdot}3 \times 1$
$CCl_3{\cdot}COOH \longrightarrow CHCl_3{\cdot}CO_2$	$1{\cdot}780 \times 10^{-16}$	—C(=O)—O—	4	$7{\cdot}1 \times$
$C_{10}H_{16} \longrightarrow C_{10}H_{16}$ (Pinene) (Dipentein)	$8{\cdot}956 \times 10^{-14}$			
$C_{10}H_{15}O{\cdot}COOH \longrightarrow C_{10}H_{16}O + CO_2$ (In water)	$2{\cdot}606 \times 10^{-14}$	—C(=O)—O—	4	$1{\cdot}04 \times 10^{-13}$
,, ,, (In benzene)	$1{\cdot}544 \times 10^{-15}$	,,	4	$6{\cdot}1 \times 10^{-15}$

In connection with the second method of procedure mentioned above, it may be pointed out that adsorption plays an important role in catalysed or " wall reactions ", in which the critical increment is really the sum of the adsorption potential (heat of adsorption) and the heat of activation (Taylor, *J. Amer. Chem. Soc.*, 1931, **53**, 578). In the present case, it is assumed that the chemically active molecules are held bound within the molecular system in the adsorbed state, and the rate of reaction is identified with the rate of ' desorption '.

By using the value of the Langmuir constant in the equation of adsorption (Kar and Ganguli, *Phys. Z.*, 1929, **30**, 918), the following expression for the velocity coefficient is obtained (*cf. Phil. Mag, loc. cit.*):

$$k_a = \frac{kT}{\rho} \cdot e^{-\frac{Q_{AB}}{RT}},$$

where $\rho = nh$ and Q_{AB} is composed of the radiant energy $Nh\nu_o$ and the heat of adsorption. For $\nu = 1$, the expression becomes identical with that of Herzfeld (*loc. cit.*). Now if ν is the average vibrational frequency of the molecules, we have $h\nu = RT$ for ordinary temperature (Ganguli, *Z. Phys.*, 1930, **64**, 81) and hence

$$k_1 = \frac{\nu}{n} \cdot e^{-\frac{h\nu_{AB}}{kT}};$$

Dushman and Christiansen's expressions).

into account the number of molecules escaping in all we have (*cf.* Polanyi and Winger, *Z. Phys. Chem.*, 432),

$$k_1 = \frac{2Q}{nNh} \cdot e^{-\frac{Q}{RT}}, = \frac{2\nu_{AB}}{n} \cdot e^{-\frac{h\nu_{AB}}{kT}}. \quad \ldots (4).$$

For the unimolecular adsorption layer ($n = 1$) (Kar and Ganguli, . *cit.*), equation (2) becomes identified with Polanyi's expression . *cit.*), while for bimolecular adsorption layer ($n = 2$), we have Dushman's expression.

Equation (4) may be obtained in a much simpler manner. If ν is requency of vibration and if the rate of reaction depends on the ion of vibrating molecules (the vibrational energy, $h\nu$ corres- ng to the critical increment), the number of active molecules ling per second (Rodebush, *J. Amer. Chem. Soc.*, 1923, **45**, is given by $dN = 2\nu\overline{N}$,

re $\overline{N}$ is the number of active molecules. Now as $h\nu$ is the rgy of activation,

$$\overline{N} = Ne^{-h\nu/kT} \text{ and hence}$$

$$k_1 = \frac{dN}{N} = 2\nu e^{-\frac{h\nu}{kT}}.$$

Expressing k_1 in the form due to Arrhenius, $k_1 = Be^{-\frac{Q}{RT}}$, the observed values of B are compared with the calculated values, $B = \frac{RT}{h}$ or $B = \nu$ or 2ν for various reactions, and entered in Table XVII.

TABLE XVII.

Reaction equation.	Q.	$\log_{10} B$.	$\log_{10} \nu$.	$\frac{kT}{h}$.	Author.
$C_3H_7N_2C_3H_7 = C_6H_{14} + N_2$	40900	13·6	14·52	13·0	Ramsperger (*J. Amer. Chem. Soc.*, 1928, **50**, 714).
$C_3H_7N_2CH_3 = C_4H_{10} + N_2$	47500	15·3	14·59	13·28 ($T=600$)	,, (*loc. cit.*).
$CH_3N_2CH_3 = C_2H_6 + N_2$	51200	16·0	14·62	——	,, (*ibid.*, 1927, **49**, 912, 1495).
$CH_3OCH_3 \longrightarrow [CH_4 + COH_2]$ $\downarrow$ $\longrightarrow CH_4 + CO + H_2$	58500	13·06	14·68	13·34 ($T=700$)	Hinshelwood and Askey (*loc. cit.*).
$C_2H_5OC_2H_5 \longrightarrow [C_2H_6 + C_2H_4O]$ $\downarrow$ $\longrightarrow C_2H_6 + CO + CH_4$	53000	11·50	14·64	13·34 ($T=700$)	Hinshelwood (*loc. cit.*).
$CH_3COCH_3 \longrightarrow CO + C_2H_6$	68500	15·20	14·75	13·457 ($T=900$)	Hinshelwood and Hutchinson (*loc. cit.*).
$CH_3CH_2COH \longrightarrow C_2H_6 + CO$	54000	12·00	15·20	13·34 ($T=700$)	Hinshelwood and Thompson (*loc. cit.*).
$CH_2OCH_2 \longrightarrow CO + CH_4$	52000	14·70	14·68	13·34 ($T=700$)	Winfield, Heckart and Mack (*loc. cit.*).
$(CH_3)_2{\cdot}CH{\cdot}CH_2Br \longrightarrow (CH_2)_3C{\cdot}Br$	6000	1·5	13·67		Dienger (*Z. Phys. Chem.*, 1928, **136**, 93).
Pinene $\xrightarrow{C_{10}H_{16}}$ Dipentein	43700	14·3	14·57	13·0 ($T=325$)	Smith (*J. Amer. Chem. Soc*, 1927, **49**, 43).
$N_2O_5 \longrightarrow [N_2O_3 + O_2] \longrightarrow N_2O_4 + \frac{1}{2}O_2$	24800	13·8	14·30	13·0 ($T=325$)	Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921 **43**, 53).
$NO_2Cl \longrightarrow = NO_2 + Cl$ $\longrightarrow 2NO_2Cl = 2NO + Cl_2$	[redacted]			13·04 ($T=370$)	Schumacher and Sprenger (*Z. Elecktrochem.*, 1929, **35**, 653).

Reaction equation.	Q.	log [redacted]	$\frac{kT}{h}$.		Author.
$C_{11}H_{16}O_3 \rightarrow C_{10}H_{16}O + CO_2$ (in water)	29700	13·1	14·38	13·04 (T=370)	Bredig and Balcom (*loc. cit.*).
$C_{11}H_{16}O_3 \rightarrow C_{10}H_{16}O + CO_2$ (in benzene)	27800	12·6	14·34	13·04 (T=370)	,, ,, ,,
,, ,, ,, (in acetophenone)	29000	13·2	14·34	13·04 (T=370)	,, ,, ,,
,, ,, ,, (in aniline)	22500	10·0	14·25	13·04 (T=370)	,, ,, ,,
$CO(NH_2)_2 \rightarrow NH_4OCN$ (in water)	32100	14·4	14·4		Fawsitt and Burrow (*J. Chem. Soc.*, 1914, 105, 615).
,, ,, ,, (in 10 p.c. alcohol)	32300	14·5	14·45		,, ,, ,,
,, ,, ,, (in 80 p.c. alcohol)	30400	13·0	14·39		,, ,, ,,
Dissociation of $CH_3{\cdot}C_2H_5{\cdot}C_5H_5CH_2{\cdot}NBr$ (in chloroform)	30000	16·7	14·38		Christiansen and Kramers (*loc. cit.*).
,, ,, ,, (in bromoform)	27700	15·2	14·36		,, ,, ,,
,, ,, ,, (in tetrachlorethane)	24300	13·6	14·30		,, ,, ,,
Dissociation of $(C_2H_5)_3SBr$	31100	16·4	14·44		v. Halban (*Z. Phys. Chem.*, 1909, 67, 129 ; 1911, 77, 719).
,, ,, ,, (in tetrachloroethane)	29300	13·3	14·38		,, ,,
,, ,, ,, (in acetic acid)	33300	17·8	14·31		,, ,,
,, ,, ,, (in amyl alcohol)	25100	14·6	14·77		,, ,,
,, ,, ,, PH_3	72000	14·00	14·30	13·44 (T=900)	Cain and Nicoll (*loc. cit.*).
$HCOOH \rightarrow H_2O$ (in 90 p.c. H_2SO_4)	48000	14·00			Trautz and Bhanderkar (*Z. anorg. Chem.*, 1919, 106, 95).

The above conclusions are based on the consideration that unimolecular reactions are brought about by radiation followed by collision, both in the case of decomposition, resembling thermionic emission as well as 'desorption'. In most cases, neither radiation nor collision is alone sufficient to bring about the reactions, although there are isolated instances (cited above), in which the heat of reaction (critical increment) is derived entirely from infra-red radiation. That infra-red frequency is absorbed by the molecules has been recently demonstrated by the beautiful work of C. V. Raman (*Indian J. Phys.*, 1928, **2**, 287) on anomalous scattering. In fact, Raman effect may be represented according to the following scheme of the general mechanism of transformation of chemical reactants proposed by Perrin (*Trans. Faraday Soc.*, 1922, **17**, 546):

$$w + \Sigma h\nu + A = A' + \Sigma h\nu' + w'.$$

The difference between the Raman effect and ordinary chemical reaction is that in the first case that molecules remain in the activated state and do not subsequently decompose, as in the latter. We may however consider Raman effect as a unimolecular chemical reaction and apply the above methods for determining the number of excited molecules. Recently the present author applied a method originating from Christiansen (*Z. Phys. Chem.* [illegible] *cit.*) for determining the number of activated molecules, and thus obtained expressions for the intensities of the Stokes [illegible] anti-Stokes lines (Communicated to *Phil. Mag.*), which agree [illegible] the results of other standard authors. Another point [illegible] mentioned in this connection. One of the objections raised [illegible] the radiation hypothesis is that the small density of the [illegible] radiation energy is unable to furnish the total energy requir[illegible] bring about the reaction. Now according to the Raman effect, even if the incident radiation do not correspond to the active frequency, this may be resolved, such that the molecules absorb the infra-red frequency ν_1, and the scattered radiation will be modified (the frequency being $\nu \mp \nu_1$). Hence, since any frequency of radiation may be scattered by the molecules, which however can retain the characteristic infra-red frequency, there can be no question as regards the deficiency of density of the activating radiation.

Summary.

The absorption of radiation for initial activation is to be associated with the rise in the energy level for vibration and rotation. This may cause the loosening of the valency electrons or widespread separation of the constituents as in dissociation. In most cases however, as has been pointed out, radiation alone is not sufficient; it supplies energy corresponding to the resonance potential. The loosely bound electrons separate, (causing disrupture of molecules), only by subsequent collision of the active molecules with the normal molecules. The total energy thus supplied corresponds to the ionisation potential, in the case of ionisation of elementary substances. Only in few cases, radiation alone is effective in bringing about the rupture of molecules; these reactions thus resemble those photochemical reactions which obey Einstein's law. In general however, the energy required for bringing about thermal unimolecular reactions is derived partly from radiation and partly from collision and the same argument may possibly be advanced for photochemical reactions as well.

CHEMICAL LABORATORY,
COLLEGE DUPLEIX,
CHANDERNAGORE.

Received August 27, 1931.

Composition of *Parkia* Oil.

By Dinker Ramchandra Paranjpe.

Oil from the seeds of *Parkia Biglandulosa*, akin to *Parkia Africana*, which is exotic but found to thrive well in Bangalore, has been examined in the present paper.

It was extracted with petroleum ether (60° to 80°) from the crushed seeds and a pale yellow oil having a peculiar odour was obtained with an yield of 16·5 g.

On examination it was found that the oil contained a fairly large amount of combined behenic acid besides the glycerides of oleic, linoleic, palmitic and stearic acids. These have been estimated quantitatively. The results show that the abnormal proportion of behenic acid as also that of unsaturated acids are somewhat unusual when the constituents of other oils are compared.

Experimental.

The analytical constants of the oil given in Table I were determined on the usual lines and are compared with the values given by Lewkowitsch (Chemical technology of oils, fats and waxes) for *Parkia Africana* which appear in the second column.

Table I.

	Parkia-Biglandulosa. (Paranjpe).	Parkia-Africana. (Lewkowitsch).
Specific gravity (15°) ...	0·9208	—
$n_D^{31\cdot3}$ ...	1·4705	—
Saponification value ...	189·5	184·0
Iodine value ...	80·87	91·6
Polensky value ...	0·25	—
Reichert-Meisel value ...	1·12	0·6
Acid value ...	5·2	—
Acetyl value ...	*nil*	—
Unsaponifiable matter ...	1·11%	—
Hehner value ...	94·7	95·5

The mixed fatty acids.—The mixed fatty acids were prepared by saponifying the oil with alcoholic solution of sodium hydroxide, the dried soap extracted with ether to remove the unsaponifiable matter, and the fatty acids regenerated from the soap by boiling with dilute hydrochloric acid. Analyses gave the following results-

TABLE II.

Mean mol. weight	290·2
Iodine value	101·6
Titre	39°·5

The mixed acids were separated into the saturated and unsaturated acids by the method of Twitchell (*J. Ind. Eng. Chem.*, 1921, **13**, 806). The process was repeated twice and the separated acids were analysed with results given below.

TABLE III.

	Saturated (30 per cent.) Acids.	Unsaturated (70 per cent.) Acids.
Eq. weight	288·0	288·0
Iodine value ...	1·2	141·5
Refractive index ...	$n_D^{65°}$ 1·4370	$n_D^{45°}$ 1·4582
Titre ...	54°·0	...

Examination of the unsaturated acids.—The additive bromo-compounds were prepared by the method of Jamieson and Baughman (*J. Amer. Chem. Soc.*, 1920, **42**, 2398). Unsaturated acids (5 g.) were dissolved in dry ether (100 c.c.) and treated with glacial acetic acid (2 c. c.). The mixture was cooled in ice and brominated with dry bromine ; on leaving in ice for six hours, no precipitate of hexa-bromide separated out showing the absence of linolinic acid. In the absence of linolinic acid the mixture of the bromides was washed with water to free it from acetic acid, and then with hypo solution to remove excess of bromine. The etherial layer was then dried with calcium chloride and finally evaporated on the water-bath. The increase in weight on bromination of the fatty acids is in fair agreement with

the proportion of oleic to linolic, worked out from the iodine value of the unsaturated acids. The bromination results are given below.

TABLE IV.

Quantity brominated ...	7·6180	5·7004 g.
Hexabromides ...	*nil.*	*nil.*
Yield of di- and tetrabromides ...	14·2845	10·7090 g.
Calculated yield according to oleic : linolic as 43·7 : 56·3 from iodine value	14·3950	10·7764 g.
M.p. of tetrabromide (cryst. from petrol) ...	118°.	118°.

The proportion of oleic to linolic thus arrived at was oleic : linolic as 43·7 : 56·3.

Examination of the saturated acids.—Saturated acids (175 g.) were collected from various separations and recoveries from the insoluble lead salts.

It was found from a qualitative test that a portion of these acids was sparingly soluble in cold ether. The acid obtained from this separation was further crystallised and was identified as behenic acid, from the molecular weight and the melting point tests. The melting point of this acid was 80-81°.

This separation was undertaken with the whole lot. A 10 p.c. ether solution of the acids was cooled to 0° and after four hours the precipitated acids were filtered and washed with cold ether. The proportion of the ether insoluble acids on the total acids was 12·8 p. c.

The ether insoluble acids had an equivalent weight of 324·3 and m.p. 73°; this corresponded to a point on the stearic-behenic acids melting point curve, where the proportion of behenic acid is 72 p. c. (Sudborough, Watson and Ayyar, *J. Indian Inst. Sci.*, 1926, **9A**, Part II, Fig. 3).

The ether soluble saturated acids were recovered and converted into methyl esters by boiling with ten times their volume of anhydrous methyl alcohol containing 4 p. c. hydrogen chloride. The purified esters were subjected to a preliminary fractional distillation under reduced pressure, and then subjected to a second fractionation at 5 mm. pressure.

The results of the refractionation are given in Table V.

TABLE V.

Fraction No.	Boiling range (5 mm.).	Yield.	Titre of ester.	M. W. of ester.	M. p. of acids.
I	175°	9·64g.	23·5°	272·0	58·0°
II	175-181	15·35	25·0°	277·7	55·5°
III	181-186	16·11	26·5°	280·6	56·0°
IV	186-188	13·94	28·9°	287·0	58·5°
V	188-195	16·97	30·3°	289·9	60·5°
VI	195-201	7·10	33·7°	302·1	60·5°
VII	201-210	11·90	37·4°	311·8	63·0°
VIII	210-220	14·27	42·4°	327·6	65·0°
IX	220-229	9·78	47·0°	340·4	73·4°
Residue	—	5·20	—	—	—

Fraction I was liquid, it was cooled to 20° to partially crystallise and then quickly filtered through a small Buchner funnel. The equivalent of the esters in the filtrate was 271, similarly the titre was not appreciably changed. The ester was then decomposed into acid and the acid crystallised from 70 p. c. alcohol. In the partial crystallisation from alcohol, the crystallised acids were filtered out and the filtrate was evaporated to obtain the lower acid. It was found to be almost pure palmitic acid from the equivalent weight determination and a mixed m.p. test with a pure specimen.

According to mixture tables (*J. Indian Inst. Sci.*, 1923, **6**, 126; Lewkowitsch, *loc. cit.*) the first five fractions seem to be mixtures of palmitic and stearic acids from the consideration of the titres and equivalent weights of the esters, and they are calculated as such.

Fraction VI has an equivalent weight of 302·1 and a titre 33·7°; if this is assumed to be a mixture of stearic with the other higher acid, which was found to be behenic acid, then according to mixture tables (*loc. cit.*) the titre should be 34° and the m.p. of the acids 66·5°, but the observed m.p. of the acids liberated from the fraction was much lower. A detailed examination of the remaining fractions showed that they were simple binary mixtures of stearic and behenic acids. The lower m.p. of fraction VI is in all probability due to traces of palmitic acid. Since no other acids excepting

palmitic, stearic and behenic are present in all the fractions, a small quantity of palmitic acid if present in fraction VI would not affect the final calculations materially ; therefore fraction VI was not subjected to any further examination.

The residue was crystallised four times from methyl alcohol and pale brown coloured flakes were obtained. The titre of the purified ester was 51·5°. The liberated acids from the above had an equivalent weight of 339·5 which did not rise on repeated crystallisations from 98 p. c. alcohol. It was therefore inferred that it was all behenic acid.

Fraction IX was carefully examined to see if any other higher acid was present. It was crystallised from methyl alcohol three times and then finally decomposed into acids. The acids were repeatedly crystallised from 98 p. c. alcohol and afterwards from cold ether. The equivalent weight did not rise above 340 and similarly the m.p. was fairly steady at 80°-81°. The mixed melting point with a pure sample of behenic acid (m.p. 80-81°) did not show any change and it was therefore nothing else but behenic acid.

Details regarding the saturated esters are summarised in Table VI.

TABLE VI.

Fraction.	Palmitic ester.	Stearic ester.	Behenic ester.
I	8·95g.	0·69 g.	...
II	11·18	4·22	...
III	9·99	6·12	...
IV	5·48	8·46	...
V	4·91	12·06	...
VI	...	6·59	0·51g.
VII	...	8·96	2·94
VIII	...	6·72	7·55
IX	...	2·39	7·39
Residue	...	...	5·20
120·26 g.	40·46	56·21	23·59
The ether insoluble portion (calculated as ester)			
17·65 g.*	...	4·95 g.	12·71
Total of saturated esters			
137·91 g.	40·46	61·15	36·30

*The percentage of the ether insoluble acids, separated previously was 12·8 per cent. in the original saturated acids ; hence the equivalent of the ether insoluble acids for 120·26 g. of the ether soluble esters works out to 17·65 g.

The unsaponifiable matter.—The unsaponifiable matter, obtained from the extraction of the dry soap with petrol ether was in a nicely crystallised condition. About one gram of the same was treated with one p. c. boiling digitonin solution. On cooling overnight a precipitate was obtained, which was filtered and weighed after drying. This gave 21·22 p. c. of sterols in the unsaponifiable matter. The acetyl derivative was prepared from the digitonin compound and crystallised from alcohol, m.p. 125·5°. This shows that sitosterol is present in the unsaponifiable matter.

The composition of the Pakira oil fatty acids works out as follows:—

Oleic acid 30·6 p.c.; linoleic acid 39·4 p.c.; palmitic acid 8·8 p.c.; stearic acid 13·8 p.c.; behenic acid 89·4 p.c.

Summary.

The oil obtained from the seeds of *Parkia Biglandulosa* (grown in Bangalore, S. India) has been examined in detail and its composition determined. It has been found that while the oil contains as much as 7·9 per cent of the behenic acid, it also contains 89·4 per cent. the unsaturated linoleic acid. The oil can therefore be used as a source of behenic acid.which is somewhat rare.

In conclusion I wish to tender my heartfelt thanks to Prof. H. E. Watson and Mr. P. R. Ayyar of the Indian Institute of Science, Bangalore, for their kind interest in this investigation.

Department of Chemistry
College of Science, Nagpur.

Received March 17, 1931.

The Bitter Principle of Neem Oil. Part I.

By Rajendra Nath Sen and Ganapati Banerjee.

The Neem tree is very plentiful in U. P. and other parts of India. Its seeds contain a high percentage of oil. The oil possesses an objectionable odour and bitter taste. It has got a high reputation for medicinal value from early times. The chemical nature of the oil was first investigated by Warden (*Phar. Indica*, Vol. I. p. 228), who found the oil to contain sulphur and removed the odorous and bitter constituents by shaking the oil with alcohol. Chatterjee (*Ind. J. Med. Res.*, 1917, **5**, 656) studied the medicinal properties of the fatty acids derived from the oil. Sen and Chatterjee (*Ind. J. Med. Res.*, 1920, **8**, 356) studied in detail and they found the characteristic acid of the oil to be 'margocic acid' belonging to the linoleic acid group (*cf.* also Ray and Dutt, *J. Soc. Chem. Ind.*, 1929, **48**, 333T). Watson, Chatterjee and Mukherjee (*J. Soc. Chem. Ind.*, 1923, **42**, 387T) worked on the odorous and bitter principle of the oil and ascribed the objectionable odour to the presence of slightly volatile organic sulphur compounds in the oil. The bitterness was also attributed to the presence of resinous acid in the form of ester in the oil.

Watson, Chatterjee and Mukherjee (*loc. cit.*) removed the bitter substance of the oil by alcohol extraction. The bitter alcoholic extract on hydrolysis gave resinous acid which proved to be the mixture of three acids of which two are bitter and one non-bitter. Both the bitter compounds were free from sulphur. During acid hydrolysis they noticed considerable quantity of sulphuretted hydrogen. During the process of purification considerable quantity of free sulphur was obtained with cold benzene.

There is every possible chance that the final sulphur free bitter acids obtained by Watson and co-workers (*loc. cit.*) when contained in the oil in the form of esters, might retain sulphur in the molecule and during the process of purification, the original compounds were decomposed liberating sulphur and sulphuretted hydrogen resulting in the bitter acids actually obtained by them.

In the present investigation, the oil was extracted with hot water and the bitter compounds isolated have been found to differ entirely

from those of Watson and co-workers (*loc. cit.*) in the fact that it contains sulphur in the molecule. It also differs from their compounds by its percentage composition and other physical and chemical properties. This substance exists in the oil chiefly in the form of soluble sodium salt. On being acidified with dilute hydrochloric acid the salt yields yellowish precipitate which turns brown on exposure. The filtrate on concentration gives crystals of sodium chloride. 100 G. of the oil yield approximately ·5 g. of the crude product.

Experimental.

Extraction and purification.—The oil was well shaken with hot water in a shaking machine several times (six or seven). The aqueous extract is then separated from the oil in a separating funnel and filtered. The filtrate on evaporation to dryness on a water-bath gave brown product which was redissolved in hot water when a portion remained insoluble (B). The solution (A) containing the Na-salt on filtration was acidified with dilute HCl when yellowish precipitate separated out (D). The solid was then dissolved in acetone and precipitated by dilution with large amount of water slightly acidulated with HCl. It was then dissolved in glacial acetic acid and reprecipitated by dilution with water. It was filtered, washed and was then successively treated with ether and benzene and then with chloroform in which a portion remained undissolved (C). It was quickly filtered in the pump and washed with chloroform. The solution on evaporation gave yellowish solid (E). The process was repeated three or four times to get the product in pure condition.

Both the substances B and D on treatment with chloroform leave a portion undissolved. The portions soluble in chloroform (E) from B and D are also identical as evident from their percentage composition and other physical and chemical properties. The portion insoluble in chloroform was altogether a different substance being free from sulphur. Thus from the crude product two distinct compounds are obtained after purification *viz.*, (1) soluble in chloroform (E) which is bitter and contain sulphur in the molecule and (2) insoluble in chloroform (C) non-bitter and sulphur free.

Action of acids and alkalis on the bitter compound (E).—It readily dissolves in cold dilute solution of sodium carbonate, and ammonia, caustic soda and potash and gives effervescence

with sodium bicarbonate. Dilute acids form brown precipitate from the alkaline solution. Concentrated sulphuric and nitric acids dissolve the substance and on dilution brown precipitate appears. Same reaction is observed with glacial acetic acid; when fused with caustic soda no characteristic reaction of the reagent is observed.

Action of other reagents: Ferric chloride imparts no characteristic coloration. Potassium permanganate is readily decolourised in the cold and bromine decolourises the chloroformic solution of the substance without evolution of hydrobromic acid.

Benzoyl chloride, acetic anhydride, sodium acetate, phenyl hydrazine and Fehling's solution have got no action on the substanee.

General properties of the bitter compound (E).—It is yellowish brown in colour. The substance is soluble in alcohol, acetone, glacial acetic acid, chloroform, pyridine and aniline; it is insoluble in water, benzene, ether, carbon disulphide and carbon tetrachloride. The substanee in the solid state does not taste bitter but does so when in solution. It contains COOH group and it is unsaturated in character. It contains no free OH but contains methoxy group. It melts with decomposition at 203-205°. (Found: C, 66·61; H, 8·15 ; S, 3·5. $C_{55}H_{81}O_{13}S$ requires C, 67·2 ; H, 8·2 ; S, 3.2 per cent.). Silver salt is prepared in the usual manner. (Found: Ag, 18·05. $C_{55}H_{79}O_{13}SAg_2$ requires Ag, 18·07 per cent.) Molecular wt. (by silver salt) is 982 and 981 (by cryoscopic method). The dibasicity of the acid has also been corroborated by the determination of neutralisation value. Methoxyl group has been determined by Zeisel's method. (Found: OMe, 13·07. $C_{51}H_{69}O_9S(OMe)_4$ requires OMe, 12·55 per cent.).

Bromo derivative is prepared by dissolving the substance ('5g) in alcohol (15 c.c.) and bromine is gradually added. When sufficient quantity of bromine has been added it is left over night. It is then heated on water-bath for 15-20 minutes and then diluted with water when insoluble bromo derivative separates out. It is then filtered, washed with hot water several times and dried. (Found: Br, 13·4. $C_{55}H_{81}O_{13}SBr_2$ requires Br, 14·0 per cent.).

From the experimental results it is thus evident that the bitter compound (E) contains two COOH, four 'OMe' and one double bond in themolecule. The exact constitution has not yet been determined.

The non-bitter compound (C).—This substance is yellowish brown in colour and does not taste bitter in solution. It exists in the

crude state in the proportion of 1:6. It is separated from the bitter substance by chloroform in which it is insoluble. It is soluble in alkalis and acids. Its solubility is the same as the bitter compound but only it is insoluble in chloroform. It decomposes above 270°. On elementary analysis the substance has been found to contain C,H and O only and does not contain sulphur unlike the bitter compound. Complete analysis of this substance was not possible for want of sufficient amount of the substance.

Conclusion.

In conclusion it may be said that the bitterness of the oil is partly due to the presence of the sodium salt of the acid (E) and partly to the presence of free acid which are held in solution in the oil. Complete extraction of the sodium salt from the oil by water does not wholly remove the bitterness of the oil and this residual bitterness is due to the presence of free bitter acid present in oil, it being sparingly soluble in water. That the residual bitterness of the oil is due to the presence of free acid can be easily verified by removing the bitterness by successive treatment of the oil with water and alcohol.

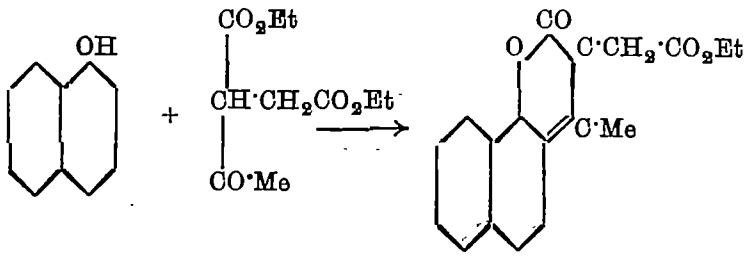
CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Received December 11, 1930

The Condensation of Ethyl Acetosuccinate with Phenols.

By Sudhir Kumar Banerjee.

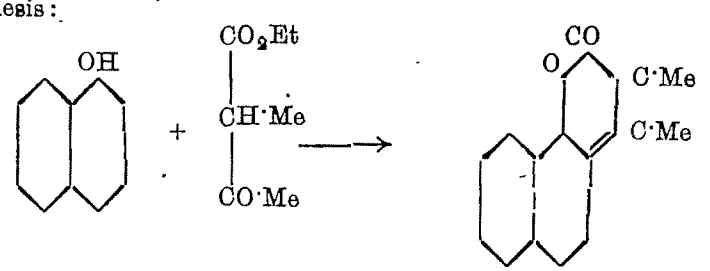
The condensation of acetoacetic esters and their alkyl derivatives with phenols has been the subject of numerous investigations (Pechmann, *Ber.*, 1884, **17**, 929, 1646, 2187; 1899, **32**, 3681; 1901, **34**, 881, 423; Biginelli, *Gazzetta*, 1895, **24**, *ii*, 492; Clayton, *J. Chem. Soc.*, 1908, **93**, 2016; Jacobson and Ghosh, *ibid.*, 1915, **107**, 424; Dey, *ibid.*, 1915, **107**, 1606). The corresponding condensation of acetosuccinic esters with phenols does not, however, appear to have been studied hitherto. In the present paper, it is shown that ethyl acetosuccinate readily enters into condensation with a variety of phenols under the customary experimental condition with the production of α-pyrone derivatives. Thus α-naphthol condenses with ethyl acetosuccinate with the formation of ethyl-4-methyl-1:2-α-naphthapyrone-3-acetate. The reaction taking place according to the following scheme: –



The constitution of the foregoing α-pyrone derivative follows from the fact that on hydrolysis it readily furnishes the corresponding monobasic acid, which when heated above its melting point is quantitatively transformed into 3:4-dimethyl-1:2-α-naphthapyrone with the elimination of carbon dioxide. As the latter substance does not appear to have been described in the literature (*cf.* Dey,

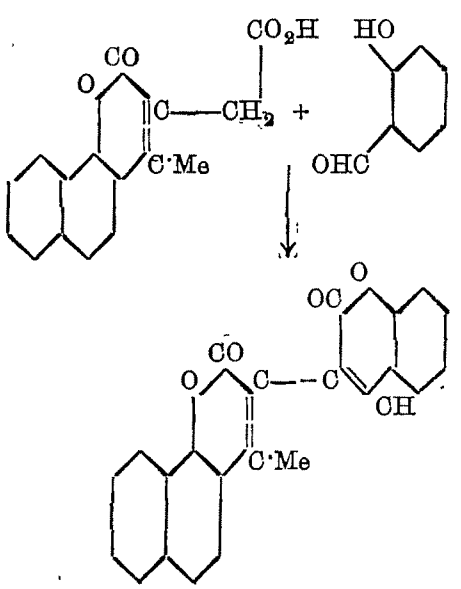
Note: While the present paper was going through the press my attention was drawn to a short note published by Y. Sankaranarayanan and A. V. Laksminarayan in the Proceedings of the Indian Science Congress, 1931, along similar lines; I undertook the work in January, 1930 and in fact the paper was written up for publication before the work of these authors was communicated. I therefore take the opportunity to place on record such results as I have obtained quite independent of these authors and leave further extension of this work to them.

loc. cit., 1608) its identity was definitely established by the following synthesis:

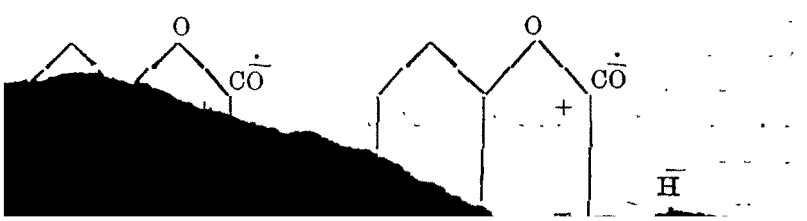


Ethyl acetosuccinate similarly condenses with resorcinol with the formation of α-pyrones, of which a number of characteristic derivatives have been prepared.

The coumarin-3-acetic esters described in this paper do not react with aromatic *o*-hydroxy aldehydes according to Knoevenagel's method. This is somewhat surprising in view of the fact, that these aldehydes condense with the corresponding coumarin-4-acetic esters, under the above conditions with remarkable ease (*cf.* Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 107). Condensation of the coumarin-3-acetic acids with hydroxyaldehydes can, however, be brought about according to Perkin's method. Thus the sodium salt of 4-methylcoumarin-1:2-α-naphthapyrone-3-acetic acid readily condenses with salicylaldehyde with the production of 4-methyl-3-(3′-coumaryl)-1:2-α-naphthapyrone as follows:



The greater reactivity of the methylene group in coumarin 4-acetic acids compared to the same grouping in the derivatives of coumarin-3-acetic acids described above, can, in the opinion of the present author, be satisfactorily explained on the basis of the principle of induced alternate polarities as developed by Lapworth (*Mem. Manchester Phil. Soc.*, 1920, **64**, *iii*, 1; *J. Chem. Soc.*, 1922, **121**, 416), and Robinson (*J. Chem. Soc.*, 1916, **109**, 1030, 1038; 1917, **111**, 959; also *Mem. Manchester Phil. Soc.*, 1920, **64**, (4), 17; *J. Chem. Soc.*, 1922, **121**, 427). The fundamental circumstance is this:—The double-linking between the carbon atoms 3 and 4 in coumarin and its derivatives is highly reactive and as such takes up the elements of bromine (Perkin, *J. Chem. Soc.*, 1871, **24**, 37), hydrocyanic acid (Bredt and Kallen, *Annalen*, 1896, **293**, 338), sodium bisulphite (*Dey* and Row, *J. Chem. Soc.*, 1924, **125**, 554), cyanoacetamide (Sheshadri, *J. Chem. Soc.*, 1928, p. 166), etc., with the greatest facility. This unsaturated centre induces alternate polarity effects in the molecule, which in the cases of the coumarin-4- and-3-acetic acids can be best represented thus:



following modification of Ruheman's method (*J. Chem. Soc.*, 1887, **71**, 330) was found to be convenient. Finely divided sodium (11·5 g.) was kept under benzene (200 c.c.) and gradually mixed with ethyl acetoacetate (65 g.) diluted with benzene (50 c.c.) the flask being cooled in ice-water during the operation. The sodio-derivative, which separated on keeping overnight, was then mixed with chloroacetic ester (62 g.) and the whole heated to boiling on the water-bath for two hours. The product was then cooled, mixed with water and the benzene layer separated, washed with water and dried with anhydrous sodium sulphate and the solvent removed. The residue of ethyl acetosuccinate on distillation under reduced pressure boiled at 150°/25 mm. (yield, 62 g.).

Condensation of ethyl acetosuccinate with α-naphthol: *Formation of ethyl 4-methyl-1:2-α-naphthapyrone-3-acetate*.—A mixture of α-naphthol (14 g.) and ethyl acetosuccinate (21g.) was cooled in ice and slowly treated with concentrated sulphuric acid (75 c.c.), the flask being vigorously shaken after each addition. The clear reddish-brown liquid, after remaining overnight, was then poured into excess of ice-water and the precipitated solid collected and thoroughly washed with cold water, after three crystallisations from dilute alcohol, the product was obtained in colourless silky needles, m.p. [illegible] yield 7g. (Found: C, 72·49; H, 5·49. $C_{18}H_{16}O$[illegible] H, 5·40 per cent.).

Hydrolysis and formatio[illegible]

The product separated from acetic acid in long white needles, m.p. 199° and found to be identical with the product described above, by analysis. (Found: C, 79·99; H, 5·52 per cent.) and by mixed m.p. 199°.

Ethyl-7-hydroxy-4-methylcoumarin-8-acetate.—Resorcinol (11 g.) was condensed with ethyl acetosuccinate (22 g.) in presence of 60 c.c. of concentrated sulphuric acid in the usual way. The product separated from a mixture of acetone and alcohol in colourless needles, m.p. 162°, yield 8 g. (Found: C, 63·69; H, 5·8. $C_{14}H_{14}O_5$ requires C, 64·12; H, 5·34 per cent.).

The *acetyl* derivative was prepared with acetyl chloride in presence of pyridine. It separated from dilute alcohol in fine leaflets, m.p. 98°. (Found: C, 62·92; H, 5·43. $C_{16}H_{16}O_6$ requires C, 63·15; H, 5·26 per cent.).

The *benzoyl* derivative was prepared by the Schotten-Baumann method in pyridine solution. It crystallised from alcohol in fine plates, m.p. 127°. (Found: C, 69·23; H, 5·23. $C_{21}H_{18}O_6$ requires C, 68·85; H, 4·92 per cent.).

The *methyl ether* was prepared by shaking the solution of the coumarin in sodium hydroxide with rather more than the calculated quantity of methyl sulphate. It crystallises from dilute alcohol in shining plates, m.p. 78°. (Found: C, 65·85; H, 5·71. $C_{15}H_{16}O_5$ requires C, 65·22; H, 5·80 per cent.).

7-Hydroxy-4-methylcoumarin-3-acetic acid was obtained by hydrolysing the above ester with alcoholic potash. It crystallises from 20 p. c. alcohol in slender needles, m.p. 268°. (Found: C, 61·13; H, 4·34. $C_{12}H_{10}O_5$ requires C, 61·54; H, 4·27 per cent.). The *silver salt* separated as a white precipitate. (Found: Ag 31·41. $C_{12}H_9O_5$ Ag, requires Ag, 31·67 per cent.).

The *anilide* of 4-methyl-α-naphthapyrone-3, acetic acid was prepared by boiling the acid (1·5 g) with aniline (5 c. c.) for 1 hour. The solid product was repeatedly washed with dilute hydrochloric acid and alcohol. It crystallises from acetic acid in silky needles, m. p. 285°. (Found: N, 3·62. $C_{22}H_{17}NO_3$ requires N, 4·08 per cent.). It is very sparinglys oluble in most organic solvents.

1:2-α-*Naphthapyrone.*—The sodium salt of 4-methyl-1:2-α-naphthapyrone-3-acetic acid (10 g.), salicylaldehyde (7 g.) and acetic anhydride (10 g.) were mixed with a trace of iodine and heated on the oil-bath at 120° for 3-4 hours and then at 180° for 2 hours. The

product thus obtained was then digested with water and filtered. It was purified from pyridine (using animal charcoal) and formed colourless crystals, m. p. 311°. (Found: C, 77·6; H, 4·05. $C_{23}H_{14}O_4$ requires C, 77·9; H, 3·9 per cent.). It is sparingly soluble in the usual organic solvents but dissolves freely in pyridine and nitrobenzene.

All attempts to condense ethyl-4-methyl-1:2-ā-naphthapyrone-3-acetate with salicylaldehyde in presence of piperidine (Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 118) were unsuccessful.

In conclusion my best thanks are due to Principal Rev. W. S. Urquhart, D. Litt., D.D., LL.D., for the facilities which he has so kindly placed at my disposal, and to Prof. B. C. Dutt, M.A., for his kind interest throughout the progress of this research.

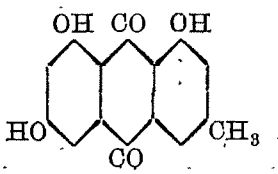
THE CHEMICAL LABORATORY,
SCOTTISH CHURCH COLLEGE,
CORNWALLIS SQUARE, CALCUTTA.

Received July 29, 1931.

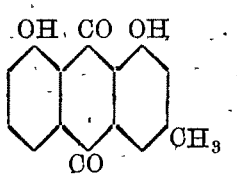
Studies in the Anthraquinone Series. Synthesis of 1 :6-Dihydroxy-and 1 :7-Dihydroxy-3-methyl-anthraquinones.

By P. C. Mitter and Nripendra Nath Chatterji.

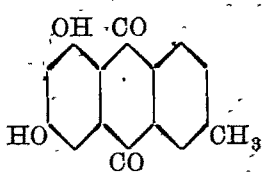
Of the three dihydroxyanthraquinones of the emodin type (Mitter and Biswas, *J. Indian Chem.* Soc., 1928, **5**, 770) only two namely, 1 :8-dihydroxy-3-methylanthraquinone (chrysophanic acid) and 6 :8-dihydroxy-3-methylanthraquinone (Marchlewski, *J. Chem. Soc.*, 1893, **63**, 1142), are known and it appeared to us of interest to synthesise 1 :6-dihydroxy-3-methylanthraquinone.



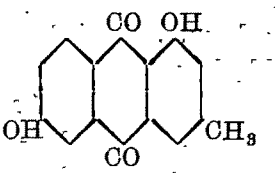
Emodin.



Chrysophanic acid.

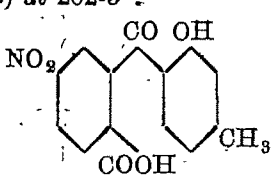


6 :8-Dihydroxy-3-methyl-anthraquione.

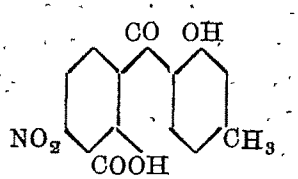


1 :6-Dihydroxy-3-methyl-anthraquinone.

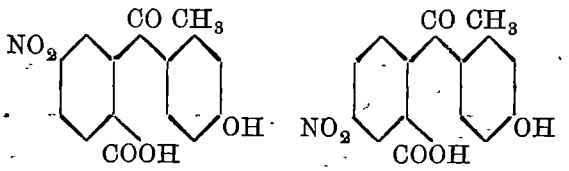
The synthesis can be effected by the condensation of 4-nitrophthalic anhydride with *m*-cresol in presence of aluminium chloride (*cf.* Eder and Widmer, *Helv. Chim. Acta*, 1922, **5**, 6). A mixture of two benzoylbenzoic acids is obtained which can be separated by fractional crystallisation. One of these (A) melts at 196° and the other (B) at 202-3°.



(I)



(II)



(III) (IV)

When phthalic anhydride or a substituted phthalic anhydride is condensed with a phenol, the condensation takes place in the *ortho* or *para* position to a hydroxyl group and we have therefore four possible formulae for the resulting products.

When the acid (A) melting at 196° is fused with caustic potash, a mixture of *p*-nitrobenzoic acid and an acid which gives a violet coloration with ferric chloride is obtained. Similarly from (B) is obtained a mixture of *m*-nitrobenzoic acid and an acid which gives a violet coloration with ferric chloride. The formation of the second acid, a derivative of salicylic acid, eliminates (III) and (IV). The constitution of the benzoylbenzoic acids (A) and (B) are therefore (I) and (II) respectively.

On reduction with ferrous sulphate and ammonia, (I) gave 4-amino-(2-hydroxy-4-methylbenzoyl)-2-benzoic acid, m.p. 218°, from which on diazotisation 4-hydroxy-(2-hydroxy-4-methylbenzoyl)-2-benzoic acid, m.p. 214-15°, was obtained. This, on ring-closure, gave 1:7-dihydroxy-3-methylanthraquinone, m.p. 255-56° (V).

Similarly from (II), 5-amino-(2-hydroxy-4-methylbenzoyl)-2-benzoic acid, m.p. 287-88°, 5-hydroxy-(2 hydroxy-4-methylbenzoyl)-2-benzoic acid, m.p. 255-56°, and 1:6-dihydroxy-3-methylanthraquinone (VII), m.p. 218-14°, were obtained.

Experimental.

4-Nitrophthalic anhydride.—This is prepared by the method of Bogert and Boroschek (*J. Amer. Chem. Soc.*, 1901, **23**, 743) with some modifications (Mitter and Sarkar, *J. Indian Chem. Soc.*, 1930, **7**, 619).

Condensation of nitrophthalic anhydride with m-*cresol.*—The anhydride (10 g.) is suspended in *m*-cresol (100 c.c.) and to this powdered aluminium chloride (20 g.) is added in small portions at a time in the course of one hour (oil-bath at 100-10°). When the addition is complete the temperature is raised to 130° and maintained at that temperature for 3-4 hours, the mixture being

mechanically stirred throughout. The contents of the flask are then acidified with 10 p.c. hydrochloric acid (135 c.c.) and the excess of *m*-cresol removed by steam distillation. The residue is digested with calcium carbonate, filtered and acidified with hydrochloric acid when a plastic mass is obtained. This is dissolved in hot methyl alcohol (charcoal) and filtered. On cooling, 4-nitro-(2-hydroxy-4-methylbenzoyl)-2-benzoic acid, m.p. 196°, crystallises out in needles, yield, 3 g. (Found: N, 4·65. $C_{15}H_{11}O_6N$ requires N, 4·65 per cent.).

A mixture of the acid (2 g.), caustic potash(10 g.) and a few drops of water is heated in a silver crucible to about 215° for 20 minutes. When cold, the mass is dissolved in water, filtered, acidified and the precipitate washed with water. It is then digested with calcium carbonate, filtered, acidified and the precipitate crystallised from water. The residue is then distilled in steam until the distillate ceases to give a violet coloration with ferric chloride, which it does in the beginning. The residue melts at 238° and the melting point is not depressed on admixture with *p*-nitrobenzoic acid. The condensation product is therefore 4-nitro-(2-hydroxy-4-methylbenzoyl)-2-benzoic acid.

5-Nitro-(2-hydroxy-4-methylbenzoyl) 2-benzoic acid (II).—The methyl alcoholic mother liquor from the preparation of (I) is evaporated and repeatedly crystallised from glacial acetic acid until its melting point becomes constant at 202-3°. It crystallises in needles. (Found: N, 4·61. $C_{15}H_{11}O_6N$ requires N, 4·65 per cent.).

On alkali fusion, the acid (II) gives *m*-nitrobenzoic acid and an acid which gives a violet coloration with ferric chloride.

4-Amino-(2-hydroxy-4-methylbenzoyl)-2-benzoic acid.—Freshly prepared ferrous sulphate (82 g.) is dissolved in water (210 c.c.), boiled and concentrated ammonia (50 c.c.) then added. To the precipitated ferrous hydroxide a warm solution of the nitroacid (4·5 g.) in concentrated ammonia (45 c.c.) is added, and the mixture boiled for 15 minutes. The filtrate is boiled to drive off ammonia and to the boiling solution, a hot solution of alum (4·5 g.) in water (45 c.c.) is gradually added and the whole filtered hot when the amino-acid crystallises out. It crystallises from alcohol in prisms melting at 218° with evolution of gas. (Found: N, 5·1. $C_{15}H_{13}O_4N$ requires N, 5·2 per cent.).

4-Hydroxy-(2-hydroxy-4-methylbenzoyl)-2-benzoic acid.—The amino acid (2 g.) is dissolved in dilute ammonia by warming and dilute

hydrochloric acid added until the precipitate first formed redissolves. The bright yellow solution of the hydrochloride is cooled to 0° and while stirring continuously by a mechanical stirrer, the calculated quantity of a solution of sodium nitrite (0·7 g.) in water (7 c.c.) is gradually added. The precipitated diazonium salt is decomposed by boiling for 15 to 20 minutes, a little animal charcoal added and the whole filtered hot, when the hydroxy acid separates in silky crystals. It is recrystallised from a mixture of ethyl acetate and petroleum ether. Rectangular plates, m.p. 214-15°. (Found: C, 65.9; H, 4·1. $C_{15}H_{12}O_5$ requires C, 66·2; H 4·4 per cent.).

1:7-*Dihydroxy*-3-*methylanthraquinone*.—To the hydroxy acid (2 g.) is added boric anhydride (2 g.) and sulphuric acid (*d*, 1·84, 4 c.c.) and then fuming sulphuric acid (20 g., 20 p.c. SO_3). The mixture is heated on the water-bath for three hours and then poured on to crushed ice when an orange mass is obtained. This is first extracted with boiling water to remove boric acid and then with cold 5 p. c. solution of sodium carbonate. The crude anthraquinone on crystallisation from glacial acetic acid gave bright yellow silky needles melting at 255-56°. (Found: C, 70·5; H, 2·7. $C_{15}H_{10}O_4$ requires C, 70·9; H 3·9 per cent.).

5-*Amino*-(2-*hydroxy*-4-*methylbenzoyl*)-2-*benzoic acid*.—The acid is obtained by reducing (II) exactly in the same manner as (I). Prisms from water, m.p. 237-38°. (Found: N, 5·2. $C_{15}H_{13}O_4N$ requires N, 5·2 per cent.).

5-*Hydroxy*-(2-*hydroxy*-4-*methylbenzoyl*)-2-*benzoic acid*.—The amino acid is diazotised as in the case of 4-amino-(2 hydroxy-4-methylbenzoyl)-2-benzoic acid. Rectangulur plates from ethyl acetate-petroleum ether mixture, m.p. 215°-16°. (Found: C, 66·3; H, 4·2. $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4 per cent.).

1:6-*Dihydroxy*-3-*methylanthraquinone*.—The ring closure is done exactly as in the case of 1:7-dihydroxy-3-methylanthraquinone. Bright yellow silky needles from glacial acetic acid, m.p. 213°-14°. (Found: C, 70·6; H, 3·6. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9 per cent.).

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA.

Received November 13, 1931.

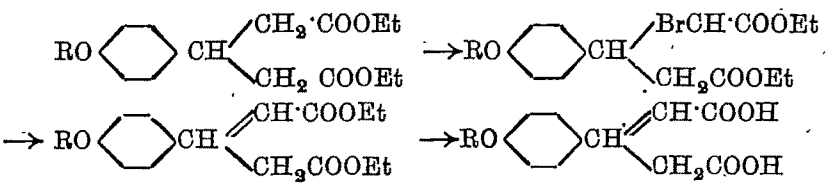
Condensation of Phenols and Phenolic Ethers with Acetone Dicarboxylic Acid. Part I. β-Substituted Glutaconic Acids.

By Vinayak Madhab Dixit.

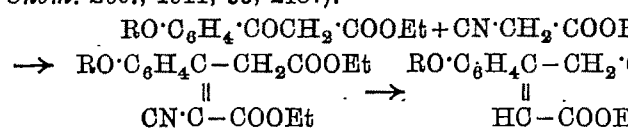
The preliminary portion of this work was done by the author in co-operation with D. B. Limaye, (*vide*, *Proc. Indian Science Congress*, 1930, p. 167). Limaye and Bhave (*J. Indian Chem. Soc.*, 1931, 8, 137), showed the formation of β-4-methoxyphenyl glutaconic acid when anisole is condensed with acetone dicarboxylic acid and studied some of its reactions. The present work is an extension of this reaction to phenol and *o*-cresolmethyl ether and deals with the establishment of the constitution of the products obtained, by direct syntheses as also several new and interesting reactions and changes which the β-substituted glutaconic acids undergo. Besides the usual dibasic acid as found by Limaye and Bhave (*loc. cit.*), a monobasic ketonic acid of which an account will be given in part II of this series, is also formed in these reactions.

The constitution of the dibasic acids as advanced by the foregoing authors, *viz.*, $R\cdot{}^{*}C(CH\cdot CO_2H)(CH_2\cdot CO_2H)$ has been confirmed by the following syntheses—

(1) from the corresponding glutaric ester (*cf.* Darbishire and Thorpe, *J. Chem. Soc.*, 1905, 87, 1714);

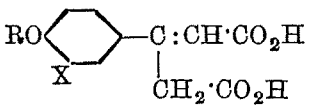


and (2) from the corresponding benzoylacetic ester (Thole and Thorpe, *J. Chem. Soc.*, 1911, 99, 2187).

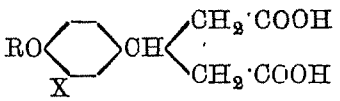


* C occupying the *para* position to the hydroxy or methoxy group.

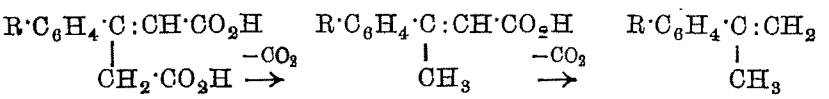
The glutaconic acids described in this paper have therefore the following constitution.



It is evident that the reduction products of the glutaconic acids should be the corresponding glutaric acids. The three glutaconic acids were therefore reduced by sodium amalgam in alkaline solution. The resulting glutaric acids, which are new, were prepared by two following synthetical processes: (*a*) condensation of *p*-hydroxybenzaldehyde with ethyl acetoacetate in presence of *p*-hydroxybenzylidenedipiperidyl and subsequent hydrolysis of the condensation product (Kotz, *J. pr. Chem.*, 1907, *ii*, **75**, 515), and (*b*) condensation of ethyl *p*-hydroxycinnamate with ethyl cyanoacetate and subsequent hydrolysis of the condensation product (Thorpe and Perkin, *J. Chem. Soc.*, 1899, **75**, 52). They have therefore the following constitution.



When reduced by phosphorus and hydriodic acid, compound from phenol gave ultimately cumol or *p*-hydroxy*iso*propylbenzene. Similar derivatives were obtained from other compounds. Each glutaric acid on heating with sodalime, eliminated two molecules of carbon dioxide and gave a cumol derivative. Such elimination of carbon dioxide from the glutaconic acids take place in stages on heating with water in a sealed tube, and immediately when boiled with 5 p.c. hydrochloric acid.



Glutaconic acid. β-Substituted crotonic acid. *iso*Propenylbenzene.

On melting, the acids eliminated one molecule of water and produced a monobasic ketonic acid identical with that obtained in the original

condensation (*loc. cit.*). Acetyl chloride acts on them in the same way. Further work in this connection will be described in the next part. The semianilides, which the acids gave with aniline, lost one molecule of water at the melting point, giving anhydrides which formed compounds with semicarbazide. The glutaconic acids absorbed two atoms of bromine when worked according to the method of Verkade and Coops (jun.) (*Rec. trav. chim.*, 1920, **39**, 586). The *laevo*-rotatory dibromide $R{\cdot}CBr{\cdot}CHBr{\cdot}CO_2H$ was isolated from the *racemic* com-

$$\begin{array}{l} \\ | \\ CH_2{\cdot}CO_2H \end{array}$$

pound through the brucine salt. The reaction between cyanoacetic ester and the glutaconic ester as carried out according to the method of Kohler and Reid (*J. Amer. Chem. Soc.*, 1925, **47**, 2803) resulted in the formation of a *p*-substituted phenylmethane triacetic acid of the general formula $R{\cdot}C_6H_4{\cdot}C(CH_2{\cdot}CO_2H)_3$. The semiammonium salts of the acids distilled after Rogerson and Thorpe (*J. Chem. Soc.*, 1905, **87**, 1691), gave corresponding pyridine derivatives. The nature of the reaction is under investigation.

$$\begin{array}{l} R{\cdot}C:CH{\cdot}CO_2H \\ | \\ CH_2{\cdot}CO_2NH_4 \end{array} \xrightarrow{2H_2O} \begin{array}{c} CH \quad COH \\ R{-}\!\!=\!\!\!>\!\!N \\ CH \quad COH \end{array}$$

Glutaconic acid. Pyridine derivative.

On fusing the *β*-4-methoxyphenylglutaconic acid with potassium hydroxide at 200°, a substituted acetophenone and a phenylacetic acid were obtained.

$$\begin{array}{l} MeO{\cdot}C_6H_4{\cdot}C:CH{\cdot}CO_2H \\ | \\ CH_2{\cdot}CO_2H \end{array}$$

↓ Glutaconic acid. ↓

$HO{\cdot}C_6H_4{\cdot}COCH_3$ $HO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$

p-Hydroxyacetophenone. *p*-Hydroxyphenylacetic acid.

The *β*-4-methoxyphenylglutaconic acid, when acted upon by 30 p.c. hydrogen peroxide in acetic acid solution, gave the methyl ether of the hydroxyphenylacetic acid identical with that obtained from potash fusion.

EXPERIMENTAL.

β-4-Hydroxyphenylglutaconic acid from (a) *phenol and acetone dicarboxylic acid.*—Powdered citric acid (25 g.) was heated with 95 p. c. sulphuric acid (75 g.) at 66° to 70° for half an hour with shaking at intervals. After cooling the mixture below 5°, phenol (10 g.) was gradually added to it with shaking, keeping the temperature below 10°. After two hours the mixture was poured over ice and allowed to stand for about three hours in a refrigerator. The glutaconic acid separated as a heavy reddish powder which was collected and washed with small quantities of sodium chloride solution. The powder was dissolved in 10 p. c. sodium hydroxide solution and was converted into its barium salt. The salt was collected, washed with little alcohol, dried and decomposed by 10 p.c. hydrochloric acid. The acid which separated on cooling, was filtered, washed and crystallised from a small quantity of water as colourless prismatic crystals, m.p. 184° (decomp.); yield 1·6 g. (Found: Eq. wt., 111·2; C, 59·42; H, 4·81. $C_{11}H_{10}O_5$ requires Eq. wt., 111; C, 59·44; H, 4·55 per cent.). *Barium salt*: (Found: Ba, 38·15. $C_{11}H_8O_5$ Ba requires Ba, 38·35 per cent.).

(b) *From the corresponding glutaric ester* (Thorpe, *J. Chem. Soc.*, 1905, 87, 1714).—Diethyl-β-4-hydroxyphenylglutarate was brominated by the method of Thrope (*loc. cit.*) to *ethyl α-bromo-β-4-hydroxyphenylglutarate*; thick brown liquid, b.p. 230°/21mm. yield 40 p. c. (Found: Br, 21·42. $C_{15}H_{19}O_5Br$ requires Br, 21·28 per cent.). This was then converted into the *glutaconic acid* by the method of Thrope (*loc. cit.*), m.p. 180° (decomp.), yield 15 p. c. Mixed m.p. with the acid obtained in (a), 182° (decomp.).

(c) *From ethyl p-hydroxybenzoylacetate.*—On condensing this with ethyl cyanoacetate according to the method of Thrope (*loc. cit.*) *ethyl α-cyano-β-4-hydroxyphenylglutaconate* was obtained as thick yellowish liquid, b.p. 269°/18mm., yield 50 p.c. (Found: C, 63·15; H, 5·55. $C_{16}H_{17}O_5$ N requires C, 63·27; H, 5·62 per cent.). This compound was then hydrolysed according to the method of Thrope (*loc. cit.*) to the glutaconic acid, m.p. 184° (decomp.), yield 12 p. c. ; Eq. wt., 111·3; mixed m.p. with the acid obtained in (a), 184° (decomp.).

β-4-Acetoxyphenylglutaconic acid was prepared by heating β-4-hydroxyphenylglutaconic acid (5 g.) with acetic anhydride (15 c.c) on a boiling water-bath. It formed rectangular prisms from ethyl acetate,

m.p. 198° (decomp.), yield 4·2 g. (Found: Eq. wt., 132·2; C, 59·2; H, 4·51. $C_{13}H_{12}O_6$ requires Eq. wt., 132; C, 59·09; H, 4·54 per cent.). *Barium salt*: (Found: Ba, 34·5. $C_{13}H_{10}O_6$ Ba requires Ba, 34·33 per cent.).

Diethyl-β-4-hydroxyphenylglutaconate.—An alcoholic solution of the glutaconic acid (10 g. in 50. c.c.) was refluxed with sulphuric acid (15 g.) on a boiling water-bath for two hours. After removal of alcohol, the residue was diluted with water and the oil which separated was extracted with ether. The ethereal extract was washed with soda solution, dried over calcium chloride and distilled; b.p. 268°/25 mm., yield 10·2 g. (Found: C, 64·88; H, 6·39. $C_{15}H_{18}O_5$ requires C, 64·75; H, 6·47 per cent.).

β-4-Hydroxyphenylglutaric Acid.

(a) *Reduction of the corresponding glutaconic acid*.—Freshly prepared sodium amalgam (1·7 g. sodium in 70 g. mercury) in small pieces, was added gradually to a *N*-caustic soda solution of *β*-4-hydroxyphenylglutaconic acid (5 g. in 40 c.c.) and the mixture shaken well after each addition, the whole addition being completed within 45 minutes. The mixture was then allowed to stand for one hour (air being excluded) when the mercury separated from it. The mixture was concentrated, boiled with animal charcoal and filtered. The solid which separated on acidifying the filtrate, was converted into the copper salt by means of copper acetate and the glutaric acid liberated by the decomposition of the copper salt by acid; white prisms from water, m.p. 172°, yield 4·4 g. It gave a greenish blue coloration with ferric chloride. (Found: Eq. wt., 111·7; C, 58·85; H, 5·3. $C_{11}H_{12}O_5$ requires Eq. wt., 112; C, 59·00; H, 5·35 per cent.).

(b) *From p-hydroxybenzaldehyde* (Method of Kotz, *loc. cit.*).—p-*Hydroxybenzylidenedipiperidyl*, white prisms from ligroin, m.p. 112,° yield, theoretical. (Found: N, 10·31. $C_{17}H_{26}ON_2$ requires N, 10·2 per cent.).

p-*Hydroxybenzylidenebisacetoacetic ester*.—White crystals from alcohol, m.p. 136°, yield 80 p. c. (Found: C, 62·6; H, 6·5. $C_{19}H_{24}O_7$ requires C, 62·7; H, 6·6 per cent.). The glutaric acid, melted at 168,° yield 25 per cent. Mixed m.p. with the acid obtained in (a), 170°.

(c) *From ethyl* -p-*hydroxycinnamate* (Method of Perkin and Thorpe, *loc. cit.*).—*Ethyl-α-cyano-β-4-hydroxyphenylglutarate*, pale

yellow liquid, b p. 184°/16 mm., yield 60 p. c. (Found: C, 62·7; H, 6·1. $C_{16}H_{19}O_5N$ requires C, 62·9; H, 6·2 per cent.). The glutaric acid, m.p. 171·5°, yield 20 per cent. Mixed m.p. with the acid obtained in (a), 172°.

Diethyl-β-4-hydroxyphenylglutarate.—An alcoholic solution of the corresponding glutaric acid (5 g. in 35 c.c. of absolute alcohol) was saturated with dry hydrochloric acid gas and refluxed in dry atmosphere on a water-bath for four hours. The alcohol was removed and the residue distilled directly ; b.p. 268°/18 mm., yield, 4·6 g. (Found: C, 64·16; H, 7·1. $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·14 per cent.).

p-Hydroxyisopropylbenzene or Cumol.

(a) *From the corresponding glutaric acid.*—An intimate mixture of powdered sodalime and *β-4-hydroxyphenylglutaric acid* (5 g.) was heated gently in a tubular retort, the volatile portion being collected in a small well cooled receiver. On keeping the receiver in a refrigerator, the contents solidified ; short needles from petroleum ether, m.p. 61°, yield 1 g. The aqueous solution gave a blue coloration with ferric chloride. (Found: C, 79·5; H, 8·75. $C_9H_{12}O$ requires C, 79·4; H, 8·84 per cent.).

(b) *By reduction of the glutaconic acid*—Red phosphorus (1·5 g.) was added in small quantities to a mixture of β-4-hydroxyphenylglutaconic acid (4 g.), glacial acetic acid (10 c.c.) and hydroiodic acid (13 g. of 4 p. c.) and the mixture refluxed for one hour. It was cooled, diluted, neutralised by sodium carbonate and filtered. The residue on the filter on extraction with ether gave cumol ; m.p. 59·5°, yield 1·2 g. Mixed m.p. with the cumol obtained in (a), 60°.

β-4-Hydroxyphenylcrotonic acid.—β-4-Hydroxyphenylglutaconic acid (7·5 g.) was heated with water (15 c.c.) in a sealed tube at 150° in an oil-bath for eight hours. On opening the tube, the contents were mixed with 10 p. c. sodium carbonate solution and distilled with steam until no volatile portion came over. The residual mixture was filtered, concentrated, boiled with animal charcoal and acidified. The solid crotonic acid which separated, gave prismatic plates from alcohol, m.p. 163°, yield 2·8 g. (Found: Eq. wt., 177·1; C, 67·5; H, 5·6. $C_{10}H_{10}O_3$ requires Eq. wt., 178; C, 67·4; H, 5·62 per cent.).

The volatile portion on purification was identified with p-*hydroxy*-iso*propenylbenzene*, m.p. 59°, yield 1 g.; benzoyl derivative m.p. 127°.

Semianilide of β-4-hydroxyphenylglutaconic acid.—A mixture of the glutaconic acid (11 g.) and dry aniline (6 g.) was refluxed at 140° in an oil-bath for eight hours. The pasty mass which separated on pouring the cold mixture into excess of hydrochloric acid (5 p. c.) became solid on grinding repeatedly with the dilute acid. It was then dissolved in sodium bicarbonate solution and filtered. The product, precipitated on acidifying the filtrate, was washed, dried and crystallised from glacial acetic acid; long yellow prisms, m.p. 197° (decomp.), yield 12·1 g. (Found: Eq. wt., 295·8; N, 4·62. $C_{17}H_{15}O_4N$ requires Eq. wt., 297; N, 4·71 per cent.).

αβ-Dibromo-β-4-methoxyphenylglutaric Acid.

(*a*) The method of Verkade and Coops (*loc. cit.*), gave colourless plates from alcohol, m.p. 121°, yield 78 p. c. (Found: Eq. wt., 197·6; Br, 40·32. $C_{12}H_{12}O_5Br_2$ requires Eq. wt., 198; Br, 40·4 per cent.).

(*b*) Bromine vapour (4·5 g.) was sucked through a solution of β-4-methoxyphenylglutaconic acid (6 g.) in glacial acetic acid (20 c.c.) by means of a water-pump. The pasty mass which separated on distilling the solution with water, solidified on washing with dilute alcohol; colourless plates from alcohol, m.p. 119°, yield 8 g.

(*c*) *The optically active antipode.*—A mixture of the alcoholic solutions of the *racemic* dibromo acid (5 g. in 50 c.c.) and brucine (5 g. in 25 c.c.) was kept in the refrigerator. The brucine salt of the *laevo*-acid separated completely after 7 hours as a crystalline powder which was washed with alcohol and crystallised saveral times with hot alcohol, m.p. 211°. (Found: N, 4·95. $C_{58}H_{64}O_{13}N_4Br_2$ requires N, 4·8 per cent.).

The precipitate of the *laevo*-acid obtained by decomposing the brucine salt with hydrochloric acid (20 c.c. of 15 p. c.) was washed with dilute hydrochloric acid until the filtrate gave no coloration with warm mercurous nitrate solution. It was then freed from acid by washing with water and was crystallised from alcohol, m.p. 123-25°, yield 2·3 g.

The *laevo*-acid (2 g.) was dissolved in absolute alcohol (50 g.) and the optical rotation of the solution was determined at 27° by using red monochromatic light. (l=20 cm. α=9·37°, M_{6100}=46·37°).

4-p-Hydroxyphenyl-2:6-dihydroxypyridine.

(a) *The semiammonium salt of the corresponding glutaconic acid.* —Pure powdered β-4-hydroxyphenylglutaconic acid (12 g.) was dissolved in ammonia (50 c.c. of 25 p. c.) and the excess of ammonia boiled off. The solution was boiled with animal charcoal, filtered and the filtrate evaporated to dryness on a water-bath; yellow crystals from alcohol, yield 13·5 g. (Found: N, 5·91. $C_{11}H_{13}O_5N$ requires N, 5·85 per cent.).

(b) *The pyridine derivative.*—The dry ammonium salt (8·5 g.) was distilled in a tubular retort under reduced pressure (40 mm.), the receiver being covered with black paper to prevent the oxidation of the pyridine compound by light. The residue was dissolved in alcohol, the alcohol removed and the residue washed with dilute alcohol and hydrochloric acid followed by a solution of ammonium bicarbonate; yellow needles from alcohol, m.p. 257°, yield 4 g. (Found: N, 6·98. $C_{11}H_9O_3N$ requires N, 6·89 per cent.). The compound turns blue on exposure to light and on melting.

Tribenzoyl derivative formed white glistening needles from acetone, m.p. 177°. (Found: N, 2·61. $C_{32}H_{21}O_6N$ requires N, 2·72 per cent.).

iso*Nitroso derivative.*—A solution of the pyridine derivative (1 g.) in sodium hydroxide (10 c.c. of 20 p.c.) was warmed with pure sodium nitrite (1 g.) and the mixture poured into acetic acid 20 c.c. of 20 p. c.). The yellowish precipitate was filtered and crystallised from alcohol, m.p. 194°, yield 0·11 g. (Found: N, 11·66. $C_{11}H_8O_4N_2$ requires N, 11·8 per cent.).

Sulphate.—A solution of the pyridine derivative (2 g.) in sulphuric acid (20 c.c. of 50 p. c.) was allowed to stand in the refrigerator overnight. The silky needles which separated, were filtered, washed and crystallised from alcohol, m.p. 320-30°.(Found: S, 6·24. $(C_{11}H_9O_3N)_2H_2SO_4$ requires S, 6·35 per cent.).

Substituted Acetophenone and Phenylacetic Acid.

p-*Hydroxyacetophenone.*—An intimate mixture of β-4-methoxyphenylglutaconic acid (10 g.)and caustic potash (13 g.) was fused in a thick retort at 200-30°. The volatile portion was collected in a receiver containing ice and water. The contents of the receiver was extracted with ether and the ethereal solution washed well with water and dilute acid. Addition of petroleum ether to the ethereal

solution gave a product which formed prismatic crystals from alcohol, m.p. 105·5°, yield 2·1 g. (Found: C, 70·6; H, 5·81. $C_8H_8O_2$ requires C, 70·5; H, 5·88 per cent.). *Semicarbazone*, m.p. 189°.

p-*Hydroxyphenylacetic acid*.—The residue in the retort was extracted with hot water and the solution, after boiling with animal charcoal and concentrating, was acidified. The precepitate was again dissolved in sodium bicarbonate solution and reprecipitated on acidifying the solution. White leaflets from dilute alcohol, m.p. 147·5°, yield 3 g. (Found: Eq. wt., 152·2; C, 63·2; H, 5·18. $C_8H_8O_3$ requires Eq. wt., 152 ; C, 63·1; H, 5·26 per cent.).

The following tables give all the compounds obtained with their characteristics and analytical results.

TABLE I.

Compounds from Anisole.

Name.	Formula.	Method of formation and yield.	Appearance and m.p. or b.p.	Analysis. Calc.	Found.
β-4-Methoxyphenylglutaconic acid. (Limaye and Bhave)	$C_{13}H_{12}O_5$	(*i*) Cond. of anisole with acetone dicarboxylic acid; yield 80 p.c. (*ii*) Methylation of the corresponding hydroxy acid. (*iii*) Thorpe's method.	White needles from hot water; m.p. 176° (decomp.).	Eq. wt., 118; C, 63·11; H, 5·19	Eq. wt., 117·9; C, 63·09; H, 5·28
The barium salt.	$C_{13}H_{10}O_5Ba$	Addition of barium chloride to the neutral sodium salt.	White crystalline powder.	Ba, 35·37	Ba, 35·15
Ethyl-α-bromo-β-4-methoxyphenylglutarate.	$C_{15}H_{21}O_5Br$	Heating the corresponding glutaric ester with PBr_5.	Yellowish thick liquid; b.p. 246°/21 mm.	Br, 21·45	Br, 21·5
Ethyl-α-cyano-β-4-methoxyphenylglutaconate.	$C_{17}H_{19}O_5N$	Thorpe's method (*loc. cit.*) yield 45 p.c.	Reddish thin liquid; b.p. 251°/21 mm.	C, 64·35 H, 5·99	C, 64·5 H, 5·91
Diethyl-β-4-methoxyphenylglutaconate.	$C_{16}H_{20}O_5$	Alcohol and dry HCl; yield 60 p.c.	Brown viscous fluorescent liquid; b.p 251°/19 mm.	C, 65·7 H, 6·88	C, 65·8 H, 6·74
β-Methoxyphenylglutaric acid.	$C_{12}H_{14}O_5$	(*i*) Reduction of the corresponding glutaconic acid; yield 70 p.c. (*ii*) Method of Parkin and Thrope; yield 15 p.c. (*iii*) Kotz's process; yield 20. p.c.	White prisms from water; m.p. 164°.	Eq. wt., 119 C, 60·5 H, 5·88	Eq. wt., 118·8 C, 60·4 H, 5·78
Ethyl-*p*-methoxybenzylidine-bisacetoacetate.	$C_{20}H_{28}O_7$	Method of Kötz.	White needles from acetone; m.p. 116°,	C, 63·5 H, 6·88	C, 63·42 H, 6·9
Ethyl α-cyano-β-4-methoxyphenyl glutarate.	$C_{17}H_{21}O_5N$	Cond. of cinnamic ester with cyanoacetic ester; yield, 65 p.c.	Thick yellow liquid; b. p.177°/20 mm.	C, 63·93 H, 6·58	C, 63·8 H, 6·49

Diethyl β-4-methoxyphenylglutrate.	$C_{18}H_{28}O_5$	Acid and alcohol with dry HCl; yield theoretical.	Thick colourless oil; b. p. 211°/18 mm.	C, 65·3 H, 7·48	C, 65·4 H, 7·4
p-Methoxyphenyl-*iso*propyl benzene.	$C_{10}H_{14}O$	(*i*) Elimination of CO_2 from the corresponding glutaric acid. (*ii*) Reduction of the glutaconic acid by P and HI; yield 35 p.c.	Liquid; b. p. 208°.	C, 80·0 H, 9·33	C, 80·15 H, 9·28
β-4-Methoxyphenyl-crotonic acid.	$C_{11}H_{12}O_3$	Heating the corresponding glutaconic acid in a sealed tube with water; yield 40 p. c.	Rectangular plates from dil. alcohol; m.p. 156°.	Eq. wt., 192 C, 68·74 H, 6·25	Eq, wt., 190·5 C, 68·8 H, 6·11
p-Methoxy*iso*propenyl benzene. (Limaye and Bhave, *loc. cit.*).	$C_{10}H_{12}O$	Action of 5 p. c HCl on the corresponding glutaconic acid; yield 70 p. c.	White leaflets from alcohol and acetone; m. p. 33°.		
Semianilide of β-4-methoxyphenylglutaconic acid.	$C_{18}H_{17}O_4N$	Heating the corresponding glutaconic acid with aniline at 150°.	Yellowish leaflets from acetic acid; m.p. 184° (decomp.).	Eq. wt., 311 N, 4·5	Eq. wt., 310·3 N, 4·55
4-*p*-Methoxyphenyl-2 : 6-dihydroxy-pyridine.	$C_{12}H_{11}O_3N$	Distilation of the ammon. salt of the glutaconic acid at 40 mm; yield 50 p. c.	Leaflets from acetic acid; m.p. 248°.	N, 6·45	N, 6·35
Benzoyl derivative of the pyridine compound.	$C_{26}H_{19}O_5N$	Action of PhCOCl and NaOH.	Light needles from methyl alcohol; m.p. 163°.	N, 3·29	N, 3·34
*iso*Nitroso derivative.	$C_{12}H_{10}O_4N_2$	Action of H_2SO_4 and $NaNO_2$ in acetic acid solution.	Yellow plates from acetone; m.p. 201°.	N, 11·33	N, 11·44
Sulphate.	$C_{24}H_{24}O_{10}N_2S$	Action of 50 p. c. H_2SO_4.	Silky needles from alcohol; m.p. 310-15°.	S, 6·05	S, 6·08
p-Methoxyphenylacetic acid.	$C_9H_{10}O_3$	Action of 30 p. c. H_2O_2 on the corresponding glutaconic acid.	Needles from dil. alcohol; m. p. 88°.	Eq. wt., 166	Eq. wt., 165·4

TABLE II.

Compounds from o-cresylmethyl ether.

Name.	Formula.	Method of formation and yield.	Appearance and m.p. or b.p.	Analysis. Calc.	Found.
β-4-Methoxy-3-methylphenylglutaconic acid.	$C_{13}H_{14}O_5$	Condensation of *o*-cresyl methyl ether with acetone dicarboxylic acid; yield 89 p. c.	White short needles from water; m.p. 173°.	Eq. wt., 125 C, 62·4 H, 5·61	Eq, wt., 124·3 C, 62·33 H, 5·54
Barium salt of the glutaconic acid.	$C_{13}H_{12}O_5Ba$	Ammon. salt and $BaCl_2$ boiled together.	White powder.	Ba, 35·58	Ba, 35·5
Diethyl β-4-methoxy-3-methylphenylglutaconate.	$C_{17}H_{22}O_5$	Alcohol and dry HCl; Yield 65 p. c.	Thick brown liquid. b.p. 265°/18 mm.	C, 66·67 H, 7·2	C, 66·7 H, 7·15
β-4-Methoxy-3-methylphenylglutaric acid.	$C_{13}H_{16}O_5$	Reduction of the glutaconic acid by Na-amalgam; yield 60 p. c.	Small prisms from alcohol, m. p. 149°.	Eq. wt., 126 C, 61·9 H, 6·4	Eq. wt., 125·6 C, 61·8 H. 6·4
Diethyl-β-4-methoxy-3-methylphenylglutarate.	$C_{17}H_{74}O_5$	yield, theoretical.	Yellow liquid b.p. 257°/14 mm.	C, 66·2 H, 7·8	C, 66·15 H, 7·7
4-Methoxy-3-methyl*iso*propylbenzene.	$C_{11}H_{16}O$	(*i*) Elimination of CO_2 from glutaric acid; yield 79 p. c. (*ii*) Reduction of the glutaconic acid by P and HI.	Yellow liquid; b.p. 231°.	C, 80·5 H, 9·76	C, 80·4 H, 9·65
4-Methoxy-3-methyl*iso*propenylbenzene.	$C_{11}H_{14}O$	Heating the glutaconic acid with 5 p. c. HCl.	Thick brown liquid; b. p. 219°/19 mm.	C, 81·6 H, 8·65	C, 81·6 H, 8·58
Semianilide of the glutaconic acid.	$C_{19}H_{19}O_4N$	Heating the glutaconic acid and aniline at 150°; yield 80 p. c.	Short needles from acetone; m.p. 201° (decomp.).	Eq. wt., 325 N, 4·31	Eq. wt., 325·8 N, 4·25

Ethyl α-cyano-β-4-methoxy-3-methylphenylmethane triacetate.	$C_{22}H_{29}O_7N$	Method of Kohler and Reid (*loc.cit.*).	Viscous reddish liquid. Pungent smell.	C, 63·0 H, 6·92	C, 62·88 H, 6·8
4-Methoxy-3-methylphenylmethane triacetic acid.	$C_{15}H_{18}O_7$	Hydrolysis of the preceeding compound; yield 20 p. c.	Short white needles from water; m.p. 191° (decomp.).	Eq. wt, 103·7 C, 58·1 H, 5·81	Eq. wt., 103·5 C, 57·95 H, 5·72
4-*p*-Methoxy-3-methylphenyl-2 :6-dihydroxypyridine.	$C_{13}H_{13}O_3N$	Yield 45 p. c.	Small yellow prisms from acetic acid; m.p. 252°.	N, 6·06	N, 6·13
Benzoyl derivative.	$C_{27}H_{21}O_5N$	Action of PhOOCl and alkali.	White needles from ethyl-acetate; m.p. 178°.	N, 3·22	N, 3·19
*iso*Nitroso derivative.	$C_{13}H_{12}O_4N$	Yield 42 p. c.	Yellow plates from acetone; m.p. 217°.	N, 10·8	N, 10·75
Sulphate.	$C_{26}H_{28}O_{10}N_2S$	Yield 50 p. c.	Flat needles; m.p. above 320°.	S, 5·73	S, 5·7
4-Hydroxy-3-methylacetophenone.	$C_{10}H_{12}O_2$	Fusion of the glutaconic acid with KOH; yield 30 p. c.	Yellowish needles; m.p. 108°.	C, 73·2 H, 7·32	C, 73·0 H, 7·25
4-Methoxy-3-methylphenylacetic acid.	$C_{10}H_{12}O_3$	Action of H_2O_2 on the glutaconic acid; yield 25 p. c.	Prismatic needles from water; m.p. 128°.	Eq. wt., 180	Eq. wt., 178·8
Dibromide of the glutaconic acid.	$C_{13}H_{14}O_9Br_2$	Bromination in acetic acid sol; yield 75 p. c.	Leaflets from chloroform; m.p. 286°.	Br, 39·72	Br, 39·9

The author expresses his thanks to Dr. A.N. Meldrum, the Principal of The Royal Institute of Science, Bombay, for his encouraging interest and advice during the course of the work and to Dr. K. G. Naik, Prof. of Chemistry, Baroda College, for obliging with appropriate suggestions to improve the paper.

ORGANIC CHEMISTRY DEPARTMENT,
ROYAL INSTITUTE OF SCIENCE,
BOMBAY.

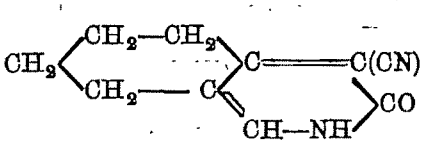
Received October 27, 1980.

Reactivity of Conjugated Systems. Part V. Condensation of Hydroxymethylene Ketones with Cyanoacetamide.

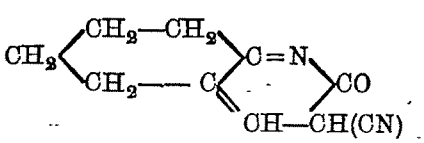
By Chittaranjan Barat.

The present work is meant to offer further support to the theory postulated in earlier papers of this series, *viz.*, that in a conjugated system, an ethylenic or acetylenic linkage exhibits a greater activity towards a reactive methylene group as contained in cyanoacetamide than a ketonic one. Whereas in the previous works, conjugated systems of the types R·CH=CH—CR′=O, (A), and R·C≡C—CR′=O, (B), have been considered, the system under examination in the present investigation consists of the type HO—CH=CH—CR=O, (C), as afforded by hydroxymethylene ketones with the dual object of establishing the mechanisms of their condensation with cyanoacetamide, and of synthesising monosubstituted hydroxypyridines.

A systematic study of these ketones dates from Wallach, (*Annalen*, 1903, **329**, 109), and seems to have ended with Sen, (*J. Chem. Soc.*, 1915, **107**, 1347) who obtained quinoline derivatives by condensing hydroxymethylene *cyclo*hexanones with cyanoacetamide. He started with the idea that the reaction would lead to an *iso*quinoline compound (I), but found that the reaction actually yielded a quinoline derivative (II).



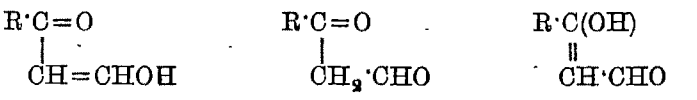
(I)



(II)

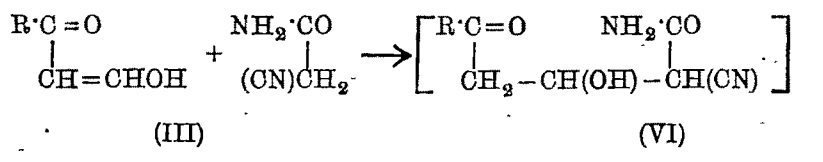
Claisen and his co-workers (*Annalen*, 1894, **281**, 331), in describing the constitution of hydroxymethylene camphor suggested

the following three possible structures for hydroxymethylene ketones in general, and,

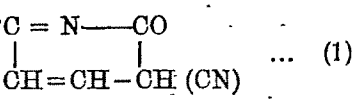


(III) (IV) (V)

Brühl (*Z. Phys. Chem.*, 1900, **35**, 1), from refractometric determinations, and Federlin (*Annalen*, 1907, **356**, 251) from colorimetric data, decided in favour of structure (III). Taking the structures (III) and (V) into consideration first, and admitting that the reactive methylene group of cyanoacetamide attaches itself to the ethylenic linkage, the reaction may take place according to equation (1) or (2) as the hydroxymethylene ketone reacts in the keto-enol phase (III) or the aldo-enol phase (V):—

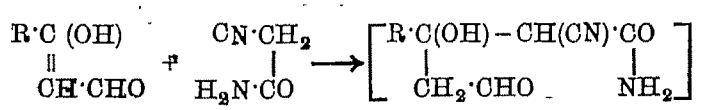


(III) (VI)

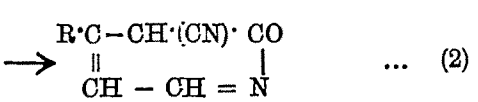


... (1)

(VII)



(V) (VIII)



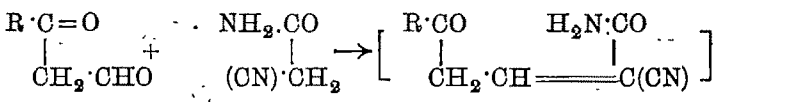
... (2)

(IX)

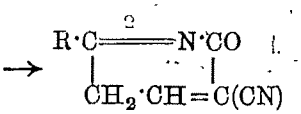
yielding a cyanopyridone of the type (VII) or (IX) respectively. But since the condensation product between hydroxymethylene acetophenone and cyanoacetamide on hydrolysis yields 2-*hydroxy*-6-*phenylpyridine* (Leben, *Ber.*, 1896, **29**, 1678), the condensation could not have taken place according to equation (2), since (IX) would have given 2-*hydroxy*-4-*phenylpyridine*. Sen's compound too would have

been an *iso*quinoline if hydroxymethylene *cyclo*hexanone had reacted in the aldo-enol phase (V).

But although the structure (V) can be so easily discarded, it is difficult to choose between the keto-enol type (III) and the keto-aldehyde type (IV) as, quite an identical product would have been obtained had the ketone reacted in the latter form, for since the aldehydic group is more active than the ketonic one, the reaction would proceed as follows:



(IV) (X)

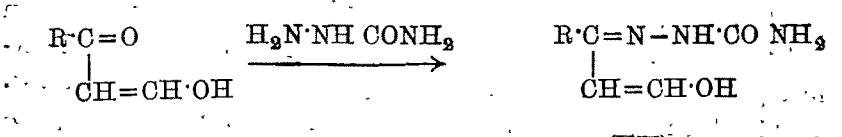


... (3)

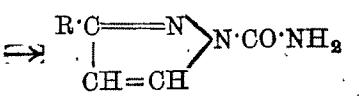
(XI)

and the condensation product (XI) would still give a 2-*hydroxy*-6-(R)-*pyridine* on hydrolysis. (*)

Wallach (*loc. cit.*) and others have also decided in favour of the keto-enol structure for hydroxymethylene ketones depending on their behaviour with semicarbazide hydrochloride and have suggested the following mechanism underlying their reaction to give rise to, first, an open chain semicarbazone (XII), and then a cyclic semicarbazone (XIII).



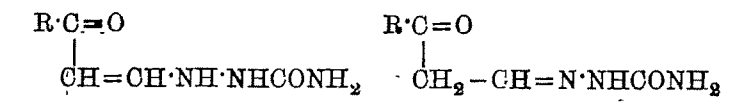
(III) (XII)



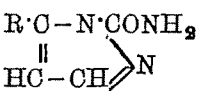
(XIII)

* It seems improbable however, that a substance would exist in an unconjugated form (IV) in preference to the conjugated one (III) since many such compounds are known to adjust themselves to a conjugated form from an unconjugated one (*cf.* Fittig, *Annalen*, 1894 **283**, 47, 269).

The weak point underlying this hypothesis is that there is room for the formation of an open chain semicarbazide derivative (XIV) or (XV) according as the constitution of hydroxymethylene ketone is represented by (III) or (IV). Both (XIV) and (XV) would give rise to the same cyclic carbonamide (XVI) distinct from the carbonamide (XIII).



(XIV) (XV)



(XVI)

Another consideration quite different from above has been brought forward by Auwers and others (*Ber.*, 1926, **58**, 2072; also *Annalen*, 1927, **452**, 182). They have isolated two cyclic carbonamide derivatives (XIII) and (XVI) depending upon whether the reaction centre of a substituted hydrazine, $NH_2 \cdot NHR$ is the imino or amino hydrogen atom. The assumption here is that the oxymethylene group is the reactive point and not the ketone, which they prove from the isomeric oximinohydrazine derivative. Under the experimental conditions of the present author, only one compound has been isolated. The open chain semicarbazide derivative from hydroxymethylene acetophenone is described by them as melting at 175-76°. This has been corroborated. The cyclic semicarbazone which they obtained in two forms corresponding to (XIII) (m.p. 142-43°) and (XVI) (m.p. 133-34°) was, however, obtained by the present author as melting at 135-37°. He has, therefore, probably had a mixture in his hands which he could not separate. Other open chain hydroxymethylene ketones were similarly treated with semicarbazide hydrochloride in presence of sodium acetate in aqueous alcoholic solution. They yielded also the three products (*vide*, experimental) monosemicarbazide, cyclic semicarbazide and a small quantity of disemicarbazide derivative. In no case, however, were the isomeric cyclic carbonamides isolated.

The conclusion from the above is that the form (IV) is inadmissible, as also (V). Hence, in all these cases, the reactivity of the ethylenic linkage in a conjugated system appears to be predominant.*

In the course of the present work, hydroxymethylene ketones have been condensed with cyanoacetamide under different conditions, and the results so far obtained have clearly pointed to the fact that the course of the primary condensation follows according to the scheme (1) given above, and have elucidated several minor complications encountered by previous workers in this direction.

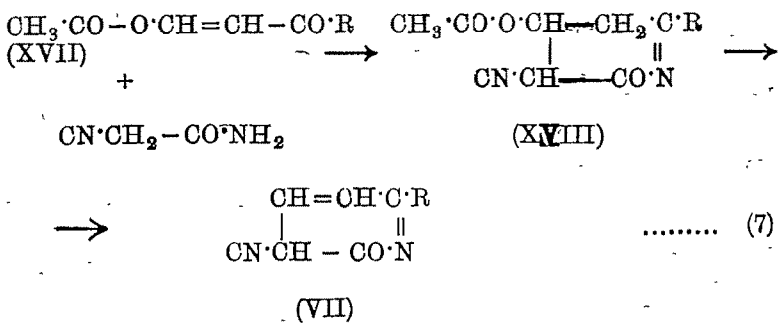
The following hydroxymethylene ketones and their derivatives have been examined in the present investigation are, (1) hydroxymethylene acetophenone, (2) hydroxymethylene *p*-methylacetophenone, (3) hydroxymethylene ethylphenylketone, and (4) hydroxymethylene methylketone. The condensations have been carried out under the following conditions.

(*a*) The condensation between the free hydroxymethylene ketones and cyanoacetamide has been carried out both with piperidine and sodium ethoxide as the condensing agents, when identical products [3 *cyano*-6-(R)-2-*pyridones*] are obtained. This latter fact, therefore, disproves the general contention that free hydroxymethylene ketones cannot be subjected to Michael's reaction on account of their acidic properties, and corroborates the hypothesis that Michael's reaction is in fact an ionic reaction (Ingold, *J. Chem. Soc.*, 1926, **128**, 1868), and since the ketones can react in the form of their sodium salts as well, there is no *a priori* reason as to why Michael's reaction could not be applied to free hydroxymethylene ketones.

(*b*) The acetyl derivatives of these hydroxymethylene ketones have been condensed with cyanoacetamide by Michael's reaction, when, unlike the case with the acetate of hydroxymethylene *cyclo*hexanone, (*cf.* Sen, *loc. cit.*) where the condensation is attended with the knocking out of the acetoxyl group, it is retained, resulting in the formation of 2-*keto*-3-*cyano*-4-*acetoxy*-6-(*R*)-2 : 3 : 4 : 5-*tetrahydropyridines* like the case with arylidene ketones (Barat, *J. Indian Chem. Soc.*, 1930, 7, 321). This discrepency between the actions of the acetates of hydroxymethylene *cyclo*ketones and of hydroxy-

* In fact it has been known from a *private communication* that a semicarbazone semicarbazide of hydroxymethylene *cyclo*hexanone was isolated by H. K. Sen (thesis for the D.Sc. degree of the London University, 1915) which also supports the enolic constitution (III) of hydroxymethylene ketones in such reaction.

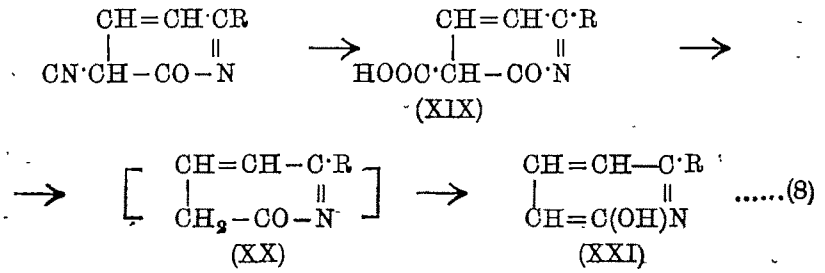
methylene ketones having a straight chain, is undoubtedly due to the difference in their respective stabilities towards alkaline media, as in Michael's reaction. When however, these condensation products, which still retain the character of an ester, are hydrolysed by alcoholic or dilute aqueous potash, they are transformed into the cyanopyridone obtained in the previous experiments. The following equation explains the whole course of reaction.



(c) The amides of these hydroxymethylene ketones formed by the action of aqueous ammonia on them, easily condense with cyanoacetamide both by heating together the two constituents, as well as by Michael's reaction, giving the same cyanopyridone as before. In the latter case however, an intermediate product of an unstable nature (containing ammonia) is formed, which is readily converted into the cyanopyridone on boiling with dilute hydrochloric acid. In both these two above cases the keto-enol phase being fixed, there can be no doubt as regards its mode of reaction.

(d) The cyanopyridones were next hydrolysed by means of fuming hydrochloric acid in the usual way ; hydrolysis with 75 p.c. sulphuric acid generally gave the carboxylic acid (XIX), which lost carbon dioxide on heating, and formed the hydroxypyridine, directly obtained by hydrolysis with fuming hydrochloric acid mentioned above. This comparative stability of the carboxylic acids is a characteristic property of these mono substituted pyridones, and must evidently be due to the absence of a substituent in an adjacent carbon atom (*cf.* the cases of disubstituted pyridones described in previous works in this series, Barat, *loc. cit.*, also *J. Indian Chem. Soc.*, 1930, 7, 851). These pyridones exhibit a hydroxylic structure only when the cyano-group is knocked off, as has also been noticed in the case

of disubstituted pyridones. Hence the structure (XXI) has been ascribed to them.



(e) Finally the condensation of these ketones with semicarbazides has been carried out but by Wallach's method as well as by the ordinary method the cyclic semicarbazone is exclusively formed, together with a very small proportion (from 5 to 10 p.c. of the total yield) of a disemicarbazone, the ordinary aqueous alcoholic medium yielded the open chain semicarbazone in the cold, and the cyclic semicarbazone, on being heated on the water-bath. This non-formation of a disemicarbazone in an alkaline (the ordinary) medium justifies the statements made previously regarding the semicarbazide condensations. Both the open chain and the cyclic semicarbazone yielded the pyrazol derivative when hydrolysed by dilute sulphuric acid.

It has further been observed that with lower members of the series, the formation of triacylbenzene derivatives is more noticeable than with the higher ones; thus, it is more marked in the case of hydroxymethylene acetophenone than with hydroxymethylene *p*-methylacetophenone (*cf.* Benary, Meyer and Charisius, *Ber.*, 1926, **59**, 109). The formation of a disemicarbazone with semicarbazide also follows this order.

Experimental.

Of the hydroxymethylene derivatives used herein, that of phenylethylketone was the stablest, while that of acetophenone the least so; the other two, having intermediate stability. Accordingly, except in the first case, they were usually preserved as their sodium (or better copper) salt, and was freshly liberated therefrom before use. Hydroxymethylene phenylethylketone could be kept undecomposed in the free condition for a pretty good length of time.

General method.—One molecule of the freshly liberated ketone and one molecule of cyanoacetamide were taken together in the aqueous alcoholic medium, the mixture cooled in ice, and a little piperidine (usually 4—5 c.c. for every tenth gram-molecule of the reactants) was then added with good shaking. The colour of the mixture deepened, and it was first left in the cold for about half an hour, and at room temperature for two to three days. Usually the condensation product separated out as a solid, but some more could be obtained on diluting and acidulating the mixture. The product usually contained a little of the triacylbenzene derivative, which was easily removed with alcohol. The cyanopyridones were freely soluble in alkalis, and strong mineral acids, and was recovered unchanged on dilution and neutralisation. Ferric chloride did not give any coloration with them. They were usually very sparingly soluble in all solvents excepting glacial acetic acid and pyridine.

The condensations by Michael's reaction were carried out in the usual way, only care was taken to keep the temperature low during the addition of the ketone to the sodiocyanoacetamide suspension; the reaction was over in a day's time and the product was separated by means of carbon dioxide after two days. The cyanopyridone so derived was identical with that obtained by the previous method.

The sodium salts of these ketones, when mixed with the molecular proportion of cyanoacetamide in aqueous solution, and treated with the usual quantity of piperidine and left over, gradually deposited the cyanopyridone in a pure form and in a very good yield in a day or two; some more could be isolated by acidulating the mother-liquor. It is interesting to note that no triacylbenzene derivative is formed in this case, even with hydroxymethylene acetophenone. The amides of these ketones were prepared in the following way:—a strong aqueous solution of ammonia was added to the ketone with good shaking till the latter went into a clear solution, it was then left over at room temperature when the amide began to separate as a heavy oil, which solidified partially or completely on allowing the excess of ammonia to evaporate spontaneously. The amide was then extracted by filtration or extraction by chloroform and isolated. It was purified by crystallisation from a mixture of petroleum ether and chloroform. It was condensed with cyanoacetamide by heating together an equimolecular mixture of the two reactants in an oil-bath held at the melting point of the mixture; ammonia was given off vigorously and gradually the melt solidified with the formation of the

cyanopyridone. It was then treated with alcohol and the condensation product being insoluble, it was easily purified from the unreacted materials and some tarry impurities. When condensed with cyanoacetamide by Michael's reaction, an intermediate compound (having a beautiful canary yellow colour) was obtained which had no sharp melting point and gradually lost ammonia on keeping and specially during any attempt at crystallisation. It was therefore converted into the cyanopyridone by boiling with dilute (1:1) hydrochloric acid for about half an hour. The product thus obtained was identical with the specimens obtained by other methods.

The acetyl derivatives of these ketones were best prepared by treating an absolute ethereal suspension of the dry sodium salt of the hydroxymethylene ketone with a slight excess of acetyl chloride, also in absolute ethereal solution, keeping the mixture well cooled in ice. Soon the cream colour of the sodium salt changed into white, with the formation of sodium chloride. The mixture was decomposed by iced water, the acetyl derivative extracted with ether, dried and isolated by evaporating the ethereal solution followed by crystallisation of the solid acetyl derivative from methyl alcohol. It was condensed with cyanoacetamide by Michael's reaction in the usual way, and was isolated best by carbon dioxide after two to three days. This could be easily converted into the original cyanopyridone by boiling with dilute 5-10 p. c. aqueous or alcoholic potash for 15-30 minutes, followed by acidulation of the alkali solution.

When any of the above condensation products were hydrolysed by 75 p.c. sulphuric acid, the carboxylic acid was invariably produced, which slowly liberated CO_2 on prolonged boiling with the sulphuric acid. If hydrolysed with fuming hydrochloric acid in a sealed tube at lower (120-25°) temperatures the carboxylic acid is the main product, while at still higher temperatures (150-60°) the hydroxypyridine is directly obtained. These carboxylic acids lose CO_2 at their melting points and yield the hydroxypyridines. These latter exhibit characteristic colorations with ferric chloride, dissolve easily in alkalis and in strong acids, and precipitate unchanged on neutralisation or dilution. They do not dissolve in carbonates, and have excellent solubilities, being soluble even in hot water to a certain extent.

With semicarbazide, the open chain semicarbazone was exclusively formed when condensed in the usual aqueous alcoholic

solution in the cold ; if the mixture was kept at the temperature of a boiling water-bath the cyclic semicarbazone was the main product. When however, the condensation was carried out in glacial acetic acid solution according to the method of Wallach (*q.v.*) the cyclic compound, mixed with a little (5—10 p. c.) of the disemicarbazone, characterised by its sparing solubility in the common organic solvents, was obtained.

The pyrazole was obtained when either of the above semicarbazones were boiled under reflux with dilute (about 25 p. c.) sulpuric acid for about 15 minutes when the solid went into complete solution with a brisk evolution of CO_2. The solution was boiled for a few minutes more and then cooled, filtered and neutralised with ammonia when the pyrazole separated out. This was isolated and crystallised usually from dilute methyl alcohol. It possessed all the properties of a pyrazole and formed well defined hydrochlorides and sulphates, which can be isolated by adding alcohol to a concentrated solution of the base in the corresponding acid; it can be crystallised without any change from dilute alcohol and is extremely soluble in water imparting an acid reaction to the solution, from which the free base separates out on the addition of ammonia or alkalis.

The general methods detailed above have been followed in all the cases cited below. In the portion that follows, therefore, only the characteristic properties of the condesation and other products have been described, the experimental details being the same in all cases have been omitted.

(A) *Condensations with Cyanoacetamide.*

I. *Hydroxymethylene acetophenone.*—The ketone was prepared by the modified method of Bülow and Sicherer (*Ber.*, 1901, **34**, 3891); and was preserved as its copper salt and was freshly liberated before use.

3-Cyano-6-phenyl-2-pyridone.—The substance was obtained in an yield of about 25 p.c. with the free ketone with piperidine, 40 p.c. by Michael's reaction, and about 60 p.c. by condensing the sodium salt in presence of piperidine. In the first of the above reactions a considerable quantity of symmetrical tribenzoyl benzene (amounting to about 50 p. c.) was formed which could be easily separated by extracting with alcohol in which it was very soluble, while the cyanopyridone was almost insoluble in it. It crystallised from dilute alcohol in fine yellow needles, m.p. 115°. (Found: C,

83·41; H, 4·83. $C_{27}H_{18}O_3$ requires C, 83·09; H, 4·62 per cent.). The cyanopyridone crystallised from pyridine or glacial acetic acid in pale yellow prismatic needles, m.p. 292-93°. (Found: N, 14·47. $C_{12}H_8ON_2$ requires N, 14·28 per cent.).

The *acetate* of the above ketone crystallised in white prismatic needles from methyl alcohol, m.p. 70-72°. It was no longer soluble in alkalis nor gave any coloration with ferric chloride. It was extremely soluble in all solvents excepting petroleum ether and water. It was easily hydrolysed into the original hydroxymethylene ketone on warming with alkalis. (Found: C, 70·05; H, 5·83. $C_{11}H_{10}O_3$ requires C, 69·47; H, 5·26 per cent.). When condensed with cyanoacetamide by Michael's reaction it gave rise to *2-keto-3-cyano-4-acetoxy-6-phenyl-2 : 3 : 4 : 5-tetrahydropyridine*. On boiling with dilute alkalis (and more slowly with dilute acids) it was easily converted into the above described cyanopyridone. It dissolved unchanged in cold alkalis from which it was recovered unchanged on acidulation. It was sparingly soluble in all solvents except pyridine and glacial acetic acid. Crystallised from either of the latter two, it was obtained in short yellow prisms, m.p. 235-36°. (Found: N, 11·15. $C_{14}H_{12}O_3N_2$ requires N, 10·93 per cent.).

Hydrolysis of the condensation products.—When any of the above condensation products were hydrolysed by sulphuric acid, the carboxylic acid, m.p. 300-02° (decomp.) was usually obtained. It crystallised from acetic acid in white felty needles that lost CO_2 on melting and was converted into the hydroxy pyridine. (Found: N, 6·73. $C_{12}H_9O_3N$ requires N, 6·51 per cent.).

6-Phenyl-2-hydroxypyridine.—This was obtained by decomposing the carboxylic acid by heat, or directly by hydrolysing any of the above condensation products by fuming hydrocloric acid in a sealed tube in the usual way. Crystallised from hot water it was obtained in light, cream coloured scales that melted at 195-96°. Its alcoholic solution gave a peculiar brownish red coloration with ferric chloride, and possessed all the properties ascribed to α-phenyl-α′-pyridone by Leben (*Ber.*, 1896, **29**, 678) who recorded an m.p. of 197° for this compound. (Found: N, 8·40. $C_{11}H_9ON$ requires N, 8·18 per cent.).

II. *Hydroxymethylene p-methylacetophenone*.—This was prepared by the method of Benary, Meyer and Charisius (*Ber.*, 1926, **59**, 108), and was preserved as the copper or sodium salt, and was freshly liberated therefrom as in the previous case.

3-*Cyano*-6-p-*tolyl*-2-*pyridone*.—The yield of this compound was nearly double that in the previous case, in all the methods of condensation described there. About 10 p.c. of *symmetrical tri*-p-*toluoylbenzene* was formed and there was very little production of any tarry impurities during all these reactions. It crystallised from dilute alcohol in cream coloured needles, m.p. 157°-58°. (Found: C, 83·12 ; H, 5·83. $C_{30}H_{24}O_3$ requires C, 83·33 ; H, 5·55 per cent.).

The cyanopyridone resembled its lower homologue in all properties and was crystallised from pyridine or glacial acetic acid in pale yellow needles melting at 297-98°. (Found: N, 13·57. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.).

The *acetate* of the hydroxymethylene ketone resembled that of the previous ketone in all properties and crystallised from methyl alcohol in white prismatic needles, m.p. at 95-96°. (Found: C, 70·81 ; H, 6·02. $C_{12}H_{12}O_3$ requires C, 70·59 ; H, 5·88 per cent.).

With cyanoacetamide it gave 2-*keto*-3-*cyano*-4-*acetoxy*-6-p-*tolyl*-2:3:4:5:-*tetrahydropyridine*, which resembled the corresponding 6-*phenyl* derivative in properties. Crystallised from acetic acid it was obtained in short yellow prisms, m.p. 258-60°. (Found: N, 10·58. $C_{15}H_{14}O_3N_2$ requires N, 10·37 per cent.).

The *amide*, prepared as detailed above, crystallised from a mixture of chloroform and petroleum ether in long yellow needles, m.p. 103°. (Found : N, 8·7. $C_{10}H_{11}ON$ requires N, 8·7 per cent.). When condensed with cyanoacetamide either by heat or by Michael's reaction it gave rise to the cyanopyridone described above in an yield of 60 to 65 p. c.

Hydrolysis of the condensation products.—When hydrolysed by sulphuric acid, all of the above condensation products were converted into the corresponding carboxylic acid, m.p. 288-90° (decomp.). (Found: N, 5·93. $C_{13}H_{11}O_3N$ requires N, 6·11 per cent.).

6-p-*Tolyl*-2-*hydroxypyridine*.—This could be prepared by any of the previously described methods which when crystallised from 40 p. c. alcohol melted at 200°, and responded to all the usual tests. (Found: N, 7·72. $C_{12}H_{11}ON$ requires N, 7·57 per cent.).

III. *With Hydroxymethylene ethylphenylketone*.—The ketone was prepared according to the method of Claisen and Meyerowitz

(*Ber.*, 1889, **22**, 3275). It was crystallised from alcohol in white needles, m.p. 118-20°.

3-*Cyano*-5-*methyl*-6-*phenyl*-2-*pyridone*.—The yield of this compound was about 75-80 p. c. even from the free ketone, the sodium salt being very pasty and hygroscopic it could not be employed. No triacylbenzene was formed from this ketone. The cyanopyridone crystallised from glacial acetic acid in pale yellow needles, m p. 264-65°. (Found: N, 13·04. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.).

The *amide* which separated at first as an oil solidified at length and crystallised from a mixture of chloroform and petroleum ether in yellow needles melting at 182-83°. (Found: N, 8·92. $C_{10}H_{11}ON$ requires N, 8·7 per cent.). It gave the above cyanopyridone under conditions described in the previous case in an yield similar to that with the free ketone.

Hydrolysis of the cyanopyridone: Formation of 2-*keto*-5-*methyl*-6-*phenylpyridine*-3-*carboxylic acid*.—This acid was stabler than the two previous ones as it was obtained both by hydrolysis with sulphuacid as also by fuming hydrochloric acid in sealed tube at comparatively high temperatures. Crystallised from diluted acetic acid it was obtained in white scales melting at 295° (decomp.). (Found: N, 6·24. $C_{13}H_{11}O_3N$ requires N, 6·11 per cent.).

5-*Methyl*-6-*phenyl*-2-*hydroxypyridine*.—The above lost CO_2 on melting and was converted into the hydroxypyridine. Crystallised from dilute methyl alcohol in white needles, m.p. 200-2°.

It gave a reddish-violet coloration with ferric chloride and responded to the other usual tests. (Found : N, 7·76. $C_{12}H_{11}ON$ requires N, 7·57 per cent.).

IV. *Hydroxymethylene methylethylketone*.—The ketone was prepared by the method of Benary, Meyer and Charisius, (*loc. cit.*) the yield being very poor.

3-*Cyano*-6-*ethyl*-2-*pyridone*.—The compound was obtained in an yield of about 40 p. c. from the free ketone both by Michael's as well as Knoevenagel's reactions. The sodium salt could not be employed on account of its hygroscopic nature. Here also no triacylbenzene was formed. Crystallised from alcohol it was obtained in short yellow needles melting at 278-80°. But for its greater solubility it resembles its other homologues in all properties. (Found: N, 19·18. $C_8H_8ON_2$ requires N, 18·92 per cent.).

Hydrolysis of the cyanopyridone : Formation of 2-keto-6-ethylpyridine-3-carboxylic acid.—It was obtained by sulphuric acid hydrolysis of the cyanopyridone as in the first two cases. Crystallised from hot water it was obtained in short white prismatic needles, m.p. 300-02°, (decomp.). (Found : N, 8·56. $C_8H_9O_3N$ requires N, 8·38 per cent.).

6-Ethyl-2-hydroxypyridine.—The carboxylic acid described above lost carbon dioxide on melting and formed the hydroxypyridine; it could also be obtained by direct hydrolysis of the cyanopridine by fuming hydrochloric acid in a sealed tube at 150-60°. It resembled the other hydryxypyridines in property and gave a sherry-red coloration with ferric chloride. It crystallised from hot water in pale yellow needles that melted at 205-06°. (Found : N, 11·61. C_7H_9ON requires N, 11·38 per cent.).

(B). *Condensations with Semicarbazide.*

I. *With Hydroxymethylene acetophenone.*—The *open chain semicarbazone* was prepared in the usual way. It was readily soluble in most solvents and was crystallised from dilute alcohol in a mass of white felty needles, m.p. 175-76° (decomp.). (Found : N, 20·27. $C_{10}H_{11}O_2N_3$ requires N, 20·49 per cent.).

The *cyclic semicarbazone* was formed by heating the ordinary reaction mixture or by Wallach's method (*loc. cit.*). It was more soluble than the above, and crystallised from dilute alcohol, m.p. 135-37°. (Found : N, 22·74. $C_{10}H_9ON_3$ requires N, 22·46 per cent.).

The *disemicarbazone* which consisted of about 10 p. c. of the total yield, when the condensation was carried out by Wallach's method, was almost insoluble in all solvents and hence could be easily separated from the cyclic semicarbazone, (which was the main product in the above reaction) by digestion with alcohol. Crystallised from hot water it melted at 225° (decomp.) (Awers and Offens found the m.p. to be 238°). (Found : N, 31·87. $C_{11}H_{14}O_2N_3$ requires N, 32·06 per cent.).

The *pyrazole* was easily obtained by hydrolysing any one of the monosemicarbazones with 25 p. c. sulphuric acid. It separated first as an oil which finally solidified, on cooling, crystallised from methyl alcohol in fine white needles, m.p. 72-74°. It was extremely soluble in all solvents excepting petroleum ether and water, and possessed all the tests ascribed to such compounds by earlier workers. (Found : N, 19·58. $C_9H_8N_2$ requires N, 19·44 per cent.).

II. *Hydroxymethylene p-methylacetophenone.*—The *open chain semicarbazone* crystallised from acetone in white felty needles melting at 182-84° (decomp.). (Fonnd : N, 18·98. $C_{11}H_{13}O_2N_3$ requires N, 19·18 per cent.).

The *cyclic semicarbazone*, obtained as before, crystallised from dilute alcohol in fine white needles, melting at 145-46°. It resembled the previously described compound in properties, and was extremely soluble in the common organic solvents. (Found: N, 21·18. $C_{11}H_{11}ON_3$ requires N, 20·9 per cent.).

The *disemicarbazone* was obtained in an yield of about 5 p. c. of the total yield when the condensation was carried out in acetic acid solution according to Wallach's method. It resembled its lower homologue in all properties, crystallised from hot water it melted at 218-20° (decomp.). (Found: N, 30·60. $C_{12}H_{16}O_2N_6$ requires N, 30·43 per cent.).

The *pyrazole* compound was obtained as usual by the hydrolysis of either the open chain or the cyclic semicarbazone described above by dilute sulphuric acid. The *sulphate*, could be obtained by adding alcohol to the acid solution, which, on crystallisation from dilute alcohol melted at 190°. (Found: N, 10·54; S, 12·81. $C_{10}H_{10}N_2$, H_2SO_4 requires N, 10·93; S, 12·5 per cent.). The free base obtained as usual by neutralisation of the acid solution with ammonia crystallised from methyl alcohol in fine white needles melting at 87-88°, and resembled the lower homologue in properties. (Found: N, 18·17. $C_{10}H_{10}N_2$ requires N 17·72 per cent.).

III. *Hydroxymethylene ethylphenylketone.*—The *open chain semicarbazone* was obtained when the condensation was carried out in the usual aqueous-alcoholic medium in the cold. Crystallised from alcohol it melted at 220° (decomp.). (Found: N, 18·94. $C_{11}H_{13}O_2N_3$ requires N, 19·18 per cent.).

The *cyclic semicarbazone* was obtained in the usual manner, and but for its slightly lesser solubility it resembled the other homologues in its properties. Crystallised from dilute methyl alcohol it was obtained in white prismatic needles, m.p. 124-25°. (Found: N, 21. $C_{11}H_{11}ON_3$ requires N, 20·89 per cent.). No *disemicarbazone* was formed with this ketone even when the condensation was carried out in acetic acid medium.

The *pyrazole*, prepared in the usual way crystallised from dilute alcohol in fine white needles, m.p. 118-20°. (Found : N, 17·58. $C_{10}H_{10}ON_2$ requires N, 17·72 per cent.).

In conclusion the author takes pleasure in expressing his grateful thanks to Prof. H. K. Sen, for his keen interest in the present investigation, and for placing all the resources of the laboratory at his disposal.

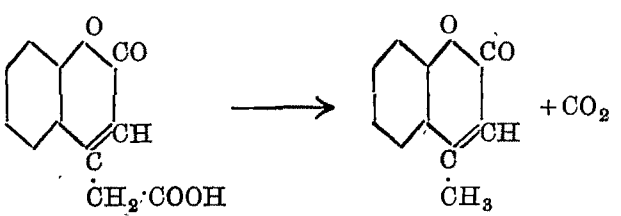
Department of Applied Chemistry,
University College of Science and Technology,
Calcutta.

Received September 1, 1931.

Coumarin-3-acetic Acids.

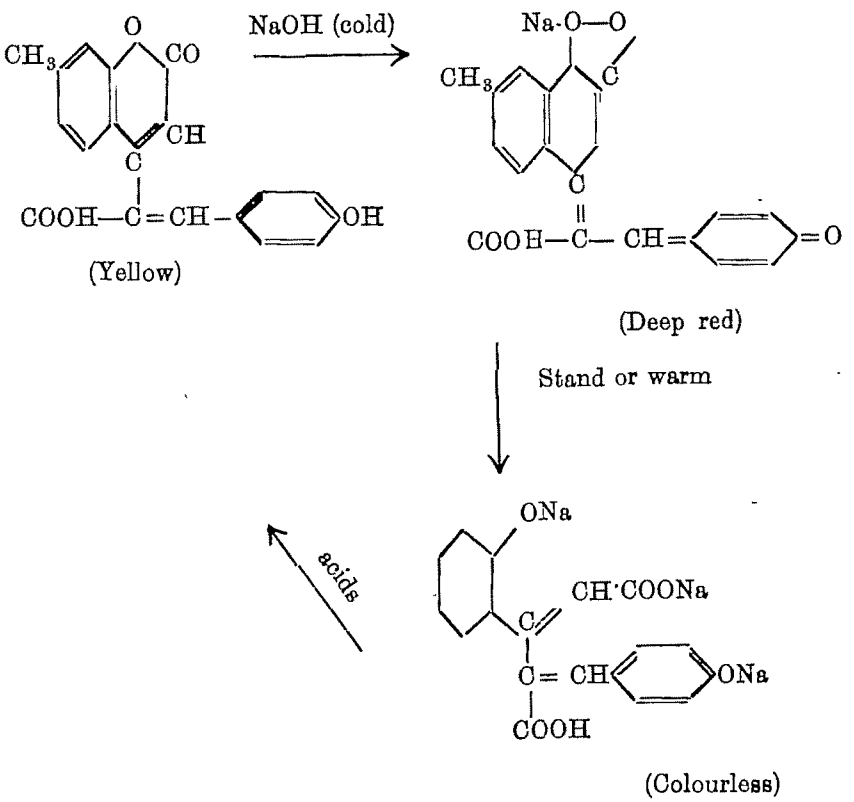
By Biman Bihari Dey and Yegnarama Sankaranarayanan.

The investigation of coumarin-4-acetic acids and their properties (Dey, *J. Chem. Soc.*, 1915, **107**, 1606) has shown that these bodies resemble malonic acid in decomposing smoothly into carbon dioxide and the corresponding 4-methylcoumarins when heated to their melting point temperatures, thus:



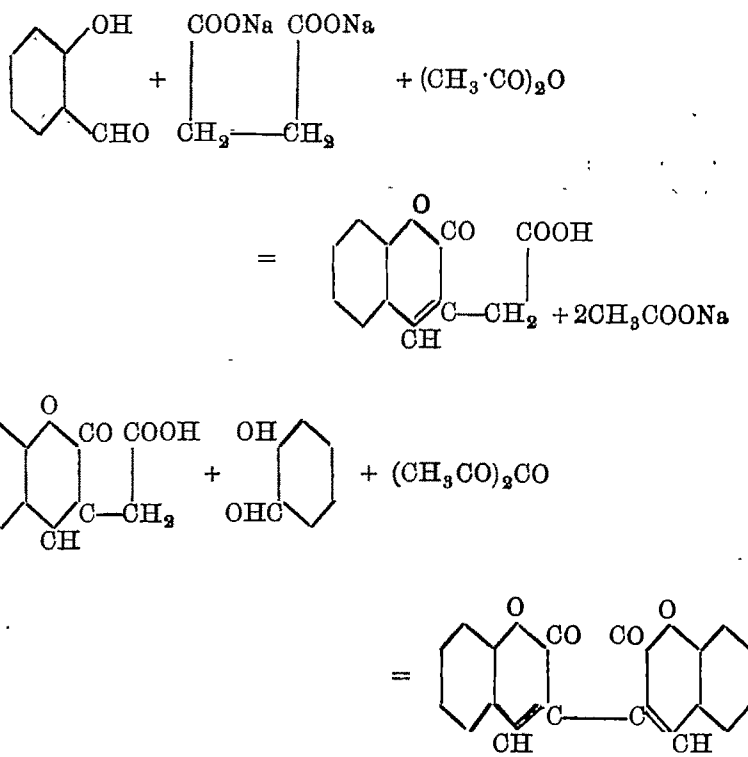
A further point of analogy between these acids and malonic acid lies in the reactivity of the methylene group (*cf.* Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 107; 1925, **2**, 227; and Dey and Seshadri, *J. Indian Chem. Soc.*, 1931, **8**, 247), the acids and their esters being found to condense readily with various aromatic aldehydes, both by Parkin's and Knoevenagel's methods, and to give rise to 4-coumarylphenyl ethylene, and 4:3-dicoumaryl derivatives. Attention was drawn in the course of these investigations to the most remarkable colour changes which occurred when alkalis acted in the cold on two of these products of condensation, *viz.*, those of 7-methylcoumarin-4-acetic acid with (*a*) *p*-hydroxybenzaldehyde, and (*b*) vanillin (Dey and Row, *J. Indian Chem. Soc.*, 1925, **2**, 280), and the view was expressed that the most plausible explanation for these phenomena probably lay in the facility with which the molecules of those compounds which had a *para*-OH group in the benzene ring

were able to tautomerise into a form that was quinonoid both in the pyrone and in the second benzene nuclei; thus:



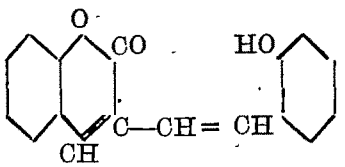
An inspection of the scheme given above would show that the quinonoid transformation should depend on the position of the acetic acid group, and that a coumarin having this group attached to position 3 of the pyrone ring, for example, would be expected to give products which would behave normally with alkalis. It appeared possible, therefore, that an investigation of the condensation of *p*-hydroxybenzaldehydes with coumarin-3-acetic acids would provide a suitable means of testing the validity of our assumption. Although the results which have so far been obtained in this direction do not permit a definite pronouncement being made on this point, much experimental data of a new and interesting type have in the meantime been collected, the publication of which it would be unwise to delay any longer.

Coumarin-3-acetic acids do not appear to have been described in literature. The reaction between salicylaldehyde and sodium succinate, which is normally expected to furnish this acid, has been studied by Dyson (*J. Chem. Soc.*, 1887, **51**, 63) who obtained only 3 : 3′-dicoumarin as the sole product of the reaction. A closer examination of this reaction has now been made and it is found that if only 1 molecule of the salicylaldehyde (and not an excess) is employed, and the experiment carried out under the same conditions as those described by Dyson (*loc. cit.*) a small amount of coumarin-3-acetic acid is also formed, and can be isolated together with the 3 : 3′-dicoumarin which still constitutes the main product of the reaction. The following equations explain the reactions that take place.

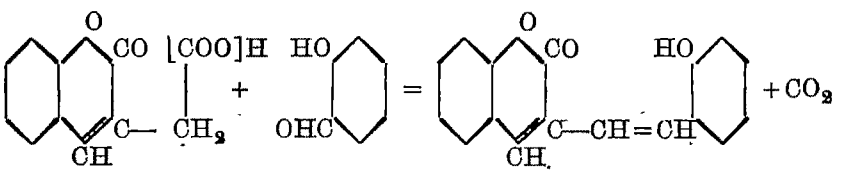


If, however, the acetic anhydride in the reaction given above be replaced by freshly made succinic anhydride, more of the coumarin acetic acid and less of the dicoumarin is formed. In a typical experiment, 6 g of salicylaldehyde yielded as much as 2·4 g. of the nearly pure coumarin-3-acetic acid, m. p. 154-55°, 2 g. of the pure

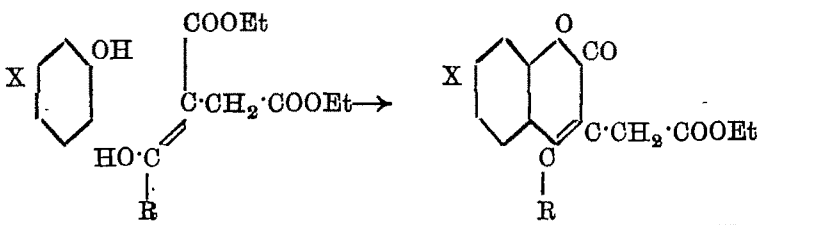
3:8′-dicoumarin (m.p. 315°), and 1·4 g. of a third product (m.p. 270°) soluble in cold alkali, which, from its chemical behaviour as well as analyses and molecular weight determinations, appears to have the structure given below.



Its formation would be readily understood if we assume that during the condensation of coumarin-3-acetic acid with salicylaldehyde, a portion of the molecules simultaneously lose carbon dioxide thus preventing the closure of the second coumarin ring, thus:



A search for other methods of obtaining coumarin-3-acetic acids has led to the discovery that members of this class may also be prepared by the condensation of phenols with either (*a*) ethyl formyl succinate or (*b*) ethyl acetosuccinate in presence of sulphuric acid. The reactions proceed in the normal manner of Pechmann's syntheses as follows: *



[R=H or CH_3].

The reaction succeeds best with phenols having a substituent group in the *meta* position, resorcinol and α-and-β-naphthols being found to give the most satisfactory results.

* A short note on this reaction was communicated to the 18th session of the Indian Science Congress held in Nagpur in January, 1931.

A noteworthy feature of the free acids is their remarkable stability, both the unsubstituted and the 4-methyl derivatives distilling unchanged at high temperatures. They present, therefore, a striking contrast with the coumarin-4-acetic acids which invariably decompase into carbon dioxide under these conditions. Although it has been possible to include in this paper only one example of the condensation of aldehydes with coumarin-3-acetic acids the methylene group in the latter has been found to be very reactive and promises to give results of considerable theoretical interest. Work in this field is now in progress and the results will be communicated shortly.

Experimental.

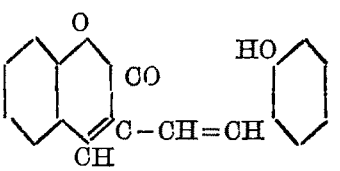
Coumarin-3-acetic acid.—Salicylaldehyde (6 g.), sodium succinate dried at 130° for several hours (11 g.) and freshly prepared succinic anhydride (14 g.) are heated in a flask fitted with an air-condenser at 170-80° for 4 hours. On cooling the yellow crystalline mass is transferred to a mortar with the aid of small amounts of hot water and triturated well with a cold solution of sodium bicarbonate (30 g. in 60 c. c. water). The major portion of the solid dissolves with evolution of CO_2, and after standing for an hour, the solution is filtered from the insoluble residue. The latter (4 g.) has deep yellow colour and melts indefinitely between 240° and 260°.

The clear filtrate is acidified with dilute HCl and allowed to stand overnight when clusters of beautiful pale yellow plates (2·4 g.) are deposited, m.p. 154-55°. A single crystallisation from boiling absolute alcohol with the addition of animal charcoal gives shining colourless plates, m.p. 150°, yield 1·8 g. (Found: C, 64·51 ; H, 4·06. $C_{11}H_8O_4$ requires C, 64·71 ; H, 3·92 per cent.).

The acid is extremely stable and shows no sign of decomposition even at 300°. On heating more strongly, it distils unchanged as a clear colourless liquid which rapidly solidifies (m.p. 158°). The equivalent weight was determined by titration with decinormal baryta. (Found: Eq. wt., 207·9. $C_{10}H_7O_2COOH$ requires Eq. wt.. 204·1).

Methylcoumarin-3-acetate is prepared by suspending the acid (2g.) in absolute methyl alcohol (30 c.c.) and saturating with hydrogen chloride until a clear solution is obtained, and then leaving for 12 hours. Colourless plates crystallise from hot alcohol, m.p. 77°. (Found: C, 66·8 ; H, 4·3. $C_{12}H_{10}O_4$ requires C, 66·05 ; H, 4·6 per cent.).

Coumarin-3-acetanilide is best prepared by boiling the free acid (1 g.) with aniline (5 c.c.) for 2 hours, washing the product with cold dilute HCl, and then with sodium carbonate, and finally crystallising from boiling alcohol. The curious observation is made that the methyl ester of the acid does not give any anilide even on prolonged boiling with aniline. The anilide forms clusters of long colourless prisms, m.p. 200°. (Found: N, 5·1. $C_{17}H_{13}O_3N$ requires N, 5·0 per cent.).

3-Coumaryl-2′-hydroxyphenyl ethylene, 

The yellow residue (m.p. 240-60°) is well ground for an hour with cold *N*-caustic soda (80 c.c.) filtered and washed. The crystalline residue, after washing with alcohol, melts sharply at 315°, yield 2g. It is practically insoluble in alcohol and the other organic solvents, dissolves only in boiling alkalis and is reprecipitated unchanged on acidification, and is fouud to be identical in all respects with Dyson's 3:3′-dicoumarin. (Found: C, 73·9 ; H, 3·7. $C_{18}H_{10}O$ requires C, 74·5 ; H, 3·45 per cent.).

On carefully acidifying the deep orange coloured filtrate from the above, a dark sticky mass separates out ; on washing with water and standing for 24 hours, it changes into a yellow crystalline solid melting rather indefinitely (170-88°). It is purified by washing thoroughly with sodium bicarbonate solution, dissolving in cold 2 *N*-caustic soda, reprecipitating with dilute HCl, and finally crystallising twice from boiling methyl alcohol with the aid of animal charcoal. Small yellow cubical crystals, m.p. 207°, yield 1·4 g. It dissolves readily in cold dilute alkalis, and decolourises bromine water and potassium permanganate solution in the cold. (Found: C, 77·1 ; H, 4·6. $C_{17}H_{12}O_3$ requires C, 77·27, H, 4·53 per cent.) M. W. (by elevation of boiling point of acetone), 274 ; $C_{17}H_{12}O_3$ requires M. W., 264.

3-Coumaryl-2′-acetoxyphenyl ethylene, prepared in the usual way by heating with acetic anhydride and a drop of pyridine, crystallises from alcohol in groups of short colourless, needles, m.p. 177°. It is insoluble in cold alkalis but is readily deacylated on warming with alkalis and reforms the hydroxy body (m.p. 207°).

7-Hydroxy-4-methylcoumarin-3-ethyl acetate.—Ethyl acetosuccinate (8 g. ; b.p. 150°/15 mm.) and resorcinol (4 g.) are mixed into a thin cream and slowly added to concentrated sulphuric acid (12 c.c.) cooled in ice. the flask being shaken vigorously after each addition. The clear liquid is kept in the ice-chamber overnight and then poured in a thin stream into 100 c.c. iced water. The precipitated solid is filtered after 2 hours, washed well with water and then with 30 c.c. alcohol, dried and crystallised from boiling alcohol. Colourless needles, are obtained m.p. 163°, yield 6 g. Its solution in dilute alkali exhibits a bright blue fluorescence characteristic of umbelliferons. (Found: C, 64·36; H, 5·43. $C_{14}H_{14}O_5$ requires C, 64·09; H, 5·38 per cent.).

7-Hydroxy-4-methylcoumarin-3-acetic acid.—The ethyl ester (m.p. 163°) is dissolved in 2*N*-caustic soda, and the solution warmed to 50-60° on the water-bath for 15 minutes. On cooling and acidifying the solution, the coumarin-3-acetic acid comes down slowly in the form of fine needles. It is crystallised once from hot 50 p.c. alcohol in colourless needles, m.p. 265°. (Found: C, 61·06; H, 4·76. $C_{12}H_{10}O_5$ requires C, 61·57; H, 4·41 per cent.).

The *silver salt* is thrown down as a curdy white precipitate. (Found: Ag, 31·04. $C_{12}H_9O_5$ Ag requires Ag, 31·6 per cent.).

The calcium and the barium salts are sparingly soluble in water, and crystallise well from the hot solutions on cooling. [Found: Ca, 5·05. $(C_{12}H_9O_5)_2$ Ca, 11 H_2O, requires Ca, 5·68 per cent. Ba, 15·40. $(C_{12}H_9O_5)_2$ Ba, 16 H_2O requires Ba, 15·37 per cent].

7-Methoxy-4-methylcoumarin-3-ethyl acetate, prepared by shaking a cold alkaline solution of 7-hydroxycoumain-3-ethyl acetate with methyl sulphate and acidifying the mixture, crystallises in colourless needles melting at 80°.

7-Methoxy-4-methylcoumarin-3-acetic acid, obtained from the above by the action of warm 2*N*-caustic soda, crystallises from 30 p.c. alcohol in colourless plates melting at 198°. (Found: Eq. wt., 231. $C_{13}H_{12}O_5$ requires Eq. wt., 248). The acid is very stable and distils unchanged at a high temperature.

7-Methoxy-4-methylcoumarin-3-methyl acetate, from the acid, methyl alcohol and hydrogen chloride, crystallises in colourless needles, m.p. 122°.

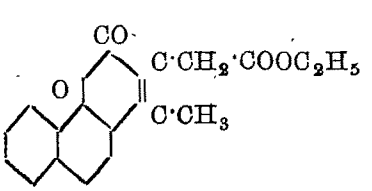
7-Acetoxy-4-methylcoumarin-3-ethyl acetate, forms colourless plates, m.p. 98°.

7-Hydroxy-4-methylcoumarin-3-acetamide.—On warming the ethyl ester with alcoholic ammonia, a yellow solution is obtained from which the free acid (m.p. 265°) can be recovered. The amide is best prepared by the method described by Buck and Perkin (*J. Chem. Soc.*, 1924, **125**, 1679). The dry acid is melted in a small flask heated to 270° in a castor oil-bath and dry ammonia gas is passed over the molten acid for 2 hours. The solid is then ground with sodium bicarbonate solution, left for half an hour, filtered and crystallised from glacial acetic acid. 0·8 G of colourless needles, m.p. 300° (decomp.) are obtained from 2 g. of the acid. (Found: N, 5·81. $C_{12}H_{11}O_4N$ requires N, 5·45 per cent.). The amide is hydrolysed on boiling for some time with 10 p. c. caustic soda, regenerating the acid (m.p. 267°).

7-Hydroxy-4-methylcoumarin-3-acetanilide.—This is obtained by boiling the acid (but not the ethyl ester) with aniline for 2 hours, pouring the liquid into dilute hydrochloric acid, washing the precipitated yellow solid with sodium bicarbonate solution, and crystallising it from alcohol in long colourless feathery needles, m p. 242°. (Found: N, 4·66. $C_{18}H_{15}O_4N$ requires N, 4·53 per cent.).

7-Acetoxy-4-methyl-3-coumaryl-3′-coumarin.—The dry sodium salt of 7-hydroxy-4-methylcoumarin-3-acetic acid (2·6 g.), salicylaldehyde (4 g.) and acetic anhydride (10 c.c.) are heated to 160-70° under reflux for 8 hours. The warm liquid is poured into 100 c.c. of ice water with vigorous stirring and the precipitated red oil washed twice by decantation. It is left in contact with a little absolute alcohol when the oil changed in the course of 24 hours into brittle mass. This is filtered, washed repeatedly with small amounts of cold alcohol in which it dissolves very sparingly, and then crystallised from boiling glacial acetic acid with the addition of animal charcoal in pale yellow prisms, m.p. 268°, insoluble in cold alkalis and sparingly soluble in most organic solvents. (Found: C, 69·01; H, 3·97. $C_{21}H_{14}O_6$ requires C, 69·6; H, 3·9 per cent.).

4-Methyl-α-naphthapyrone-3-ethyl Acetate.



α-Naphthol (4 g.) and ethyl acetosuccinate (7 g.) are condensed in presence of cold concentrated sulphuric acid, and the product worked up in the usual manner. The ester crystallises from methyl alcohol in long colourless needles, m.p. 139°, yield 2 g. (Found : C, 72·95 ; H, 5·56. $C_{18}H_{16}O_4$ requires C, 72·97 ; H, 5·45 per cent.).

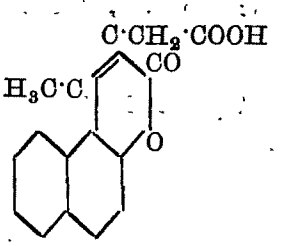
4-Methyl-α-naphthapyrone-3-acetic acid.—The ethyl ester (1 g.) is boiled with 2*N*-caustic soda (20 c.c.) until the solid dissolves completely (about half an hour). The cold solution is filtered and acidified when a white precipitate is immediately formed. It is purified by dissolving in sodium bicarbonate, reprecipitating with acid, and crystalllising the dry precipitate from hot glacial acetic acid in colourless shining plates, m.p. 251°. (Found: Eq. wt., 273. $C_{16}H_{12}O_4$ requires Eq. wt., 268).

The *silver salt* is precipitated as a pale yellow microcrystalline powder. (Found: Ag, 28·8. $C_{16}H_{11}O_4Ag$ requires Ag, 28·8 per cent.).

The *calcium* and the *barium salts* are thrown down as crystalline precipitates on adding calcium and barium chloride to a neutral solution of the acid.

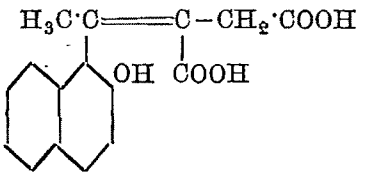
4-Methyl-α-naphthapyrone-3-acetanilide.—The curious observation made in the case of the 7-hydroxycoumarin derivative is repeated here ; the ethyl ester does not react with aniline even on prolonged boiling. The anilide is made from the free acid by the method described before. Boiling with 20 p.c. caustic soda for 15 minutes reconverts it into the acid, m.p. 251°. (Found: N, 4·8. $C_{22}H_{17}O_3N$ requires N, 5·08 per cent.).

4-Methyl-β-naphthapyrone-3-acetic Acid.



This acid and not the expected ethyl ester, is formed on condensing β-naphthol and ethyl acetosuccinate in the usual manner. The product crystallises from alcohol in pale yellow needles, m.p. 199°. (Found: Eq. wt., 272·9. $C_{16}H_{12}O_4$ requires Eq. wt., 268).

ββ-Methyl-2-hydroxynaphthylitaconic Acid.

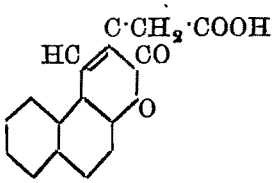


β-Naphthapyrone-3-acetic acid (m.p. 199°, 2 g.) is dissolved in 26 c.c. of 2*N*-caustic soda and the solution boiled for half an hour. On cooling and acidifying the solution it becomes turbid and then soft colourless plates, refracting light like jewels, slowly separate out. After an hour the crystals are filtered, washed with cold water, and dried on porous plate. They melt sharply at 154° giving off steam and then solidify again. The residue which melts at 198° is identified with 4-methyl-β-naphthapyrone-3-acetic acid by a mixed melting point. Boiling with alcohol or acetic acid is also found to result in ring closure, the acid (m.p. 198°) crystallising after some time. A 50 p. c. methyl alcoholic solution of the itaconic acid was exposed to direct sunlight for 4 hours but no change was observed, the acid (m.p. 154°) being thrown down on addition of water. It is curious to note, however, that on leaving the alcoholic solution in the dark overnight, the β-naphthapyrone-3-acetic acid (m.p. 198°) crystallises out, showingthat ring closure had been effected even in the cold in the dark. (Found: Eq. wt., 142·5. $C_{16}H_{14}O_5$ requires Eq. wt., 143).

4-Methyl-β-naphthapyrone-3-ethyl acetate. prepared by esterifying the acid, forms hard colourless prisms, m.p. 101°. The ester, on hydrolysis with hot or even cold alkali, gives the itaconic acid (m.p. 150°), which, on heating, changes into the stable acetic acid (m.p. 198°). (Found: C, 73·6; H, 5·3. $C_{18}H_{16}O_4$ requires C, 73·0 ; H, 5·4 per cent.).

4-Methyl-β-naphthapyrone-3-methyl acetate crystallises in short colourless prisms, m.p. 137°.

β-Naphthapyrone-3-acetic Acid.



β-naphthol (5·6 g.) and ethyl formylsuccinate (8 g.) are mixed and added to cold sulphuric acid in the usual way. On pouring the liquid after 24 hours into excess of water, a red oil separates which is washed several times by decantation with cold decinormal alkali. It changes into a yellow semi-solid mass but does not completely solidify. It is therefore hydrolysed by boiling with 2*N*-caustic soda until a clear solution is obtained, filtered and acidified, when a sticky resinous mass is precipitated which becomes granular on standing in contact with water for 24 hours. It is purified by dissolving in cold sodium bicarbonate solution, filtering from a small amount of insoluble matter, precipitating with hydrochloric acid and finally crystallising twice from boiling methyl alcohol in colourless rectangular plates, m.p. 265°. (Found: Eq. wt., 258. $C_{15}H_{10}O_4$ requires Eq. wt., 254).

β-naphthapyrone-3-methyl acetate, prepared from the acid by esterification with methyl alcohol and hydrogen chloride, crystallises from methyl alcohol in long prismatic needles, m.p. 149°. (Found: C, 70·51 ; H, 4·22. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·47 per cent.).

PRESIDENCY COLLEGE, MADRAS.

Received November 12, 1931.

Review

Anorganisch-chemisches Praktikum (Qualitative Analyse und Anorganische Praparate)—by Dr. E. H. Riesenfeld, a. o. Professor of Chemistry, University of Berlin. Tenth edition. pp. 398. Published by S. Hirzel, Leipzig.

The book under review has passed through ten editions in about twenty years, which speaks for its great popularity in Germany. It deals mainly with inorganic preparations and qualitative analysis. The subject matter has been arranged very carefully, so that beginners may find their initiation as smooth and interesting as possible. Sixty typical and important preparations are described in the book and are distributed judiciously over the whole text but are concentrated mainly in the beginning of qualitative practices. These latter, unlike the procedure followed in ordinary text books, begin with the tests for anions or acid radicles.

A short section has been devoted to the elementary theoretical considerations underlying the practical methods. Theoretical ideas of a more advanced character are also met with, being disseminated throughout the analytical and preparative exercises. Tables of separation (analytical) are drawn up in a considerably abbreviated form by the use of ionic symbols and formulæ. These and certain other abbreviations so often met with in the book may appear somewhat confusing to some.

Reactions described under individual ions are fairly exhaustive. Figures showing the appearance of crystals under the microscope of some analytically important substances are given at proper places and these cannot but be both useful and instructive.

Though apparently intended for the beginners, the book will be of help even to the more advanced students. It can be confidently recommended to all chemistry students preparing for their University degrees.

P. R.